

# *Analytical Abstracts*

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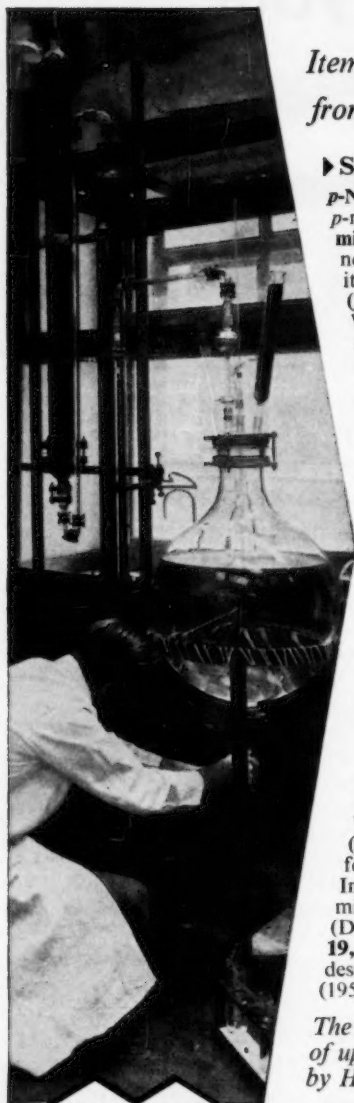
### ► Uranium by spectrophotometry

Our 1-(2-pyridylazo)-2-naphthol (PAN for short), already known as a metal indicator for complexometric titrations. (H. Flaschka and H. Abdine, *Mikrochim. Acta*, **770** (1956); *Anal. Abs.*, **4**, 794 (1957)) is now described as a spectrophotometric reagent of high specificity for uranium (H. Shibata, *Anal. Chim. Acta*, **22**, 479 (1960)).

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**5134. Complexometric titrations with diethylenetriaminopenta-acetic acid.** E. Wänninen. *Acta Acad. Aboensis, Math. et Phys.*, 1960, **21** (17), 1-110 (in English).—The dissociation constants of diethylenetriaminopenta-acetic acid (I) and the stability constants of a number of its metal chelates have been determined at 25° and an ionic strength of 0.1. The complexes with Ba, Ca, Cd, Cu, Hg<sup>II</sup>, Li, Mg, Ni, Sr and Zn had higher stability constants than those with EDTA. Binuclear complexes, in which the ratio of metal to reagent is 2:1, are formed with many metals, and are of unusually high stability; this may interfere in the titration of a metal ion with I, but such interference was not observed in alkaline soln. Since I is a pentabasic

acid, an increase in the acidity of the soln. causes a large decrease in the "conditional constant" of the complex (i.e., the constant obtained by taking side-reactions into account), so that I forms weaker complexes with most metals in slightly acid soln. than does EDTA. A nomogram and auxiliary diagrams are given from which the conditional constants of the complexes of certain metals with I, EDTA, 1:2-diaminocyclohexane-NNN'-tetra-acetic acid, 1:2-di-(2-aminoethoxy)ethane-NNN'-tetra-acetic acid, triaminotriethylamine and triethylenetetramine can be calculated. A second nomogram permits the calculation of the concn. of metal at the end-point, and of the error in the complexometric titration of one metal in the presence of another. I is often more efficient than EDTA for the titration of several metals in alkaline soln. It is particularly useful for the titration of Ba<sup>2+</sup> and (indirectly) of SO<sub>4</sub><sup>2-</sup>, and is more suitable than EDTA for the titration of Ce in acid soln.

R. E. E.

**5135. Specific masking by acetylacetone in titrations with ethylenediaminetetra-acetic acid.** W. Z. Jablonski and E. A. Johnson (Hopkin and Williams Ltd., Chadwell Heath, Essex, England). *Analyst*, 1960, **85**, 297-299.—The cations completely or partly masked by acetylacetone under the conditions used for titrating Zn or Pb with EDTA, with xylenol orange as indicator, are listed. For the determination of Zn or Pb in the absence of other metals, the neutral or slightly acid soln. is treated with 5 N HNO<sub>3</sub> and sufficient hexamine to produce a pH of 5 to 6, and then titrated with 0.1 M EDTA, with xylenol orange as indicator. In the presence of Be, Pd or Al, acetylacetone is added before the hexamine buffer. In the presence of Fe or U, the soln., acidified with 5 M HNO<sub>3</sub>, is oxidised with H<sub>2</sub>O<sub>2</sub> (unless Fe is absent), acetylacetone is added before, and nitrobenzene after, the hexamine buffer and the mixture is shaken to extract the coloured metal complex. Xylenol orange is added to the diluted soln. and the aq. layer is titrated with 0.1 M EDTA without removal of the nitrobenzene. To determine Bi in the presence of Mo, acetylacetone is added to the strongly acidified soln. and, after the Mo complex has completely pptd., the pH is adjusted to 1 to 1.5 with 5 N NaOH (or 5 N aq. NH<sub>3</sub>), the indicator is added and the liquid is titrated. To restore the fading colour near the end-point, drops of alkali are added. A. O. JONES

**5136. Trace analysis by X-ray fluorescence using ion-exchange resins.** J. N. van Niekerk and J. F. de Wet (National Physical Res. Lab., Pretoria, S. Africa). *Nature*, 1960, **186**, 380-381.—The method described involves a concentration step similar to that of Grubb and Zemany (*Ibid.*, 1955, **176**, 221), but the elements to be determined are collected on a granular or liquid ion-exchange resin, which is then irradiated directly in an X-ray spectrograph. Rapid equilibrium is attained provided that solid resins are soaked beforehand; if the variation in particle size of the resin is small no extra variance is introduced by distributional variations in the resin bed. Absorption and enhancement effects due to co-adsorbed elements, if present, can be overcome by the use of suitable internal standards. With solid resins the limit of detection of U under these conditions is 0.1 p.p.m. K. A. PROCTOR

**5137. Elementary analysis by X-ray fluorescence.** A. Hans (Centre Nat. de Rech. Met., Belgium). *Ind. Chim. Belge*, 1960, **25** (4), 353-358.—The principles of X-ray emission and fluorescence

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**5132. 1-(2-Thiazolylazo)-2-hydroxyaryl compounds as complexometric metal indicators.** B. S. Jensen (Atomic Energy Comm., Rise, Denmark). *Acta Chem. Scand.*, 1960, **14** (4), 927-932 (in English).—1-(2-Thiazolylazo)-2-naphthol and its 6-sulphonic acid, 2-(2-thiazolylazo)-*p*-cresol, 6-(2-thiazolylazo)-resorcinol (I) and -orcinol (II), and 3-dimethylamino-6-(2-thiazolylazo)phenol (III) are prepared and shown to form intensely coloured chelates in neutral or slightly acidic soln. with Th<sup>4+</sup>, La<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>. All dyes except I and II are also pH indicators. All act as indicators in the direct EDTA titration with Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> in acetate or pyridine buffers, and with Zn<sup>2+</sup> and Pb<sup>2+</sup> in pyridine buffer. The accuracy for 0.1 M soln. is within  $\pm 1\%$ . Titration of Cd<sup>2+</sup>, Th<sup>4+</sup>, Zr<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> was unsatisfactory. Colour changes (listed) were readily observed with all dyes except III. J. P. STERN

**5133. Analytical applications of complexones. XI. The action of oxidising agents on EDTA and the possibility of its potentiometric evaluation.** F. Bermejo Martínez and R. Rey Mendoza. *An. Real Soc. Esp. Fis. Quim.*, B, 1959, **55**, 309-314.—The effects of KMnO<sub>4</sub>, Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in an acid medium, and of KMnO<sub>4</sub> in an alkaline one, on EDTA (disodium salt) are studied. Several methods for its potentiometric determination are proposed. The variation of the oxidation potential with the pH of EDTA is studied and the experimental results are interpreted. CHEM. ABSTR.

**5134. Complexometric titrations with diethylenetriaminepenta-acetic acid.** E. Wänninen. *Acta Acad. Aboensis, Math. et Phys.*, 1960, **21** (17), 1-110 (in English).—The dissociation constants of diethylenetriaminepenta-acetic acid (I) and the stability constants of a number of its metal chelates have been determined at 25° and an ionic strength of 0.1. The complexes with Ba, Ca, Cd, Cu, Hg<sup>II</sup>, Li, Mg, Ni, Sr and Zn had higher stability constants than those with EDTA. Binuclear complexes, in which the ratio of metal to reagent is 2:1, are formed with many metals, and are of unusually high stability; this may interfere in the titration of a metal ion with I, but such interference was not observed in alkaline soln. Since I is a pentabasic

acid, an increase in the acidity of the soln. causes a large decrease in the "conditional constant" of the complex (i.e., the constant obtained by taking side-reactions into account), so that I forms weaker complexes with most metals in slightly acid soln. than does EDTA. A nomogram and auxiliary diagrams are given from which the conditional constants of the complexes of certain metals with I, EDTA, 1:2-diaminocyclohexane-NNN'-tetra-acetic acid, 1:2-di-(2-aminoethoxy)ethane-NNN'-tetra-acetic acid, triaminotriethylamine and triethylenetetramine can be calculated. A second nomogram permits the calculation of the concn. of metal at the end-point, and of the error in the complexometric titration of one metal in the presence of another. I is often more efficient than EDTA for the titration of several metals in alkaline soln. It is particularly useful for the titration of Ba<sup>2+</sup> and (indirectly) of SO<sub>4</sub><sup>2-</sup>, and is more suitable than EDTA for the titration of Ce in acid soln. R. E. E.

**5135. Specific masking by acetylacetone in titrations with ethylenediaminetetra-acetic acid.** W. Z. Jablonski and E. A. Johnson (Hopkin and Williams Ltd., Chadwell Heath, Essex, England). *Analyst*, 1960, **85**, 297-299.—The cations completely or partly masked by acetylacetone under the conditions used for titrating Zn or Pb with EDTA, with xylenol orange as indicator, are listed. For the determination of Zn or Pb in the absence of other metals, the neutral or slightly acid soln. is treated with 5 N HNO<sub>3</sub> and sufficient hexamine to produce a pH of 5 to 6, and then titrated with 0.1 M EDTA, with xylenol orange as indicator. In the presence of Be, Pd or Al, acetylacetone is added before the hexamine buffer. In the presence of Fe or U, the soln., acidified with 5 M HNO<sub>3</sub>, is oxidised with H<sub>2</sub>O<sub>2</sub> (unless Fe is absent), acetylacetone is added before, and nitrobenzene after, the hexamine buffer and the mixture is shaken to extract the coloured metal complex. Xylenol orange is added to the diluted soln. and the aq. layer is titrated with 0.1 M EDTA without removal of the nitrobenzene. To determine Bi in the presence of Mo, acetylacetone is added to the strongly acidified soln. and, after the Mo complex has completely pptd., the pH is adjusted to 1 to 1.5 with 5 N NaOH (or 5 N aq. NH<sub>3</sub>), the indicator is added and the liquid is titrated. To restore the fading colour near the end-point, drops of alkali are added. A. O. JONES

**5136. Trace analysis by X-ray fluorescence using ion-exchange resins.** J. N. van Niekerk and J. F. de Wet (National Physical Res. Lab., Pretoria, S. Africa). *Nature*, 1960, **186**, 380-381.—The method described involves a concentration step similar to that of Grubb and Zemany (*Ibid.*, 1955, **178**, 221), but the elements to be determined are collected on a granular or liquid ion-exchange resin, which is then irradiated directly in an X-ray spectrograph. Rapid equilibrium is attained provided that solid resins are soaked beforehand; if the variation in particle size of the resin is small no extra variance is introduced by distributional variations in the resin bed. Absorption and enhancement effects due to co-adsorbed elements, if present, can be overcome by the use of suitable internal standards. With solid resins the limit of detection of U under these conditions is 0.1 p.p.m. K. A. PROCTOR

**5137. Elementary analysis by X-ray fluorescence.** A. Hans (Centre Nat. de Rech. Met., Belgium). *Ind. Chim. Belge*, 1960, **25** (4), 353-358.—The principles of X-ray emission and fluorescence



spectroscopy are reviewed and the ranges of atomic wt. (Ti to Mo) and concn. for which they may usefully be employed are discussed. Methods of minimising and correcting for absorption of exciting and fluorescence radiation by other elements present are discussed; the preparation of a 10-g borax "bead" containing from 0.1 to 0.2 g of sample, giving the effect of massive dilution by a single known "impurity," is described in detail. Examples of applications, with references, are given. E. J. H. BIRCH

**5138. Recent developments in polarography.** G. W. C. Milner (Anal. Chem. Branch, A.E.R.E., Harwell, Berks., England). *Chimia*, 1960, **14** (4), 106-111 (in English).—Cathode-ray, square-wave and pulse-polarographic techniques are reviewed and the last two methods are compared. Recent suggestions which may lead to the conversion of the current peaks found in oscillographic polarography from the asymmetric type to the flat-topped type observed in conventional polarography are mentioned and the single-sweep oscillographic polarograph is described. (15 references.)

E. G. CUMMINS

**5139. General procedure in the low-temperature wet-oxidation of organic compositions. Perchloric and periodic acids as oxidants. "The periodic acid liquid fire reaction."** G. F. Smith and H. Diehl (Noyes Lab., Univ. Illinois, Urbana, U.S.A.). *Talanta*, 1960, **4** (3), 185-193.—Periodic acid has been substituted for  $\text{HNO}_3$  in the original  $\text{HClO}_4$ - $\text{HNO}_3$  "liquid fire reaction" (Smith, *Brit. Abstr. C*, 1953, 519). For specific reactions this offers the advantages of lower reaction temp. and more effective degradation of large organic molecules. The effective oxidation potentials are in the range 1.6 to 2.0 V. The procedures for cellulose, wool, sugars, leather, coal and polymers are given. The temp. needed are  $<200^\circ$  and less concentrated  $\text{HClO}_4$  soln. (66 to 70%) are now required, so that there is no tendency towards uncontrolled reaction rates.

R. M. S. HALL

## 2.—INORGANIC ANALYSIS

*General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.*

**5140. Polarographic analysis. I. Polarography of copper, uranium and iron in alkaline solutions containing triethanolamine.** I. M. Issa and R. M. Issa (Cairo Univ. and Nat. Res. Centre, Egypt). *Z. anal. Chem.*, 1960, **174** (4), 254-260 (in English).—Copper, Fe and U were polarographed in various electrolytes, alone and in the presence of each other. The electrolytes studied were NaOH with triethanolamine (I), acetate buffer of pH 5 with I, and ammonium carbonate with I or EDTA. Each could be used for the determination of Cu alone. For Cu together with Fe, best results were obtained by addition of EDTA to all the electrolytes (including  $\text{NH}_4\text{Cl}$ -aq.  $\text{NH}_3$ ) except to NaOH with I. When Cu, Fe and U were present together, only ammonium carbonate with EDTA gave waves suitable for analytical use.

P. D. PARR-RICHARD

**5141. Investigation of the anion-exchange method for the separation of indium, tin, antimony and tellurium with radioactive indicators.** I. Stroński

(Inst. Nuclear Res., Polish Acad. Sci., Kraków). *Roczn. Chem.*, 1960, **34** (2), 709-712.—In the separation of small quantities of In, Sb and Sn, In, Te and Sn, or Sb, Te and Sn, a column (2 mm  $\times$  80 to 110 mm) of the strongly basic anionite IRA-400 was used, with  $^{115\text{m}}\text{In}$ ,  $^{124}\text{Sb}$ ,  $^{125}\text{Sb}$ ,  $^{127\text{m}}\text{Te}$  and  $^{113,115}\text{Sn}$  as indicators. Indium and Sb were eluted with 3 N HCl, Te with N HCl and Sn with 2 N  $\text{HClO}_4$  at a pressure-regulated rate of 0.04 ml per min. The method described enables carrier-free  $^{125}\text{Sb}$  and  $^{115\text{m}}\text{In}$  to be obtained and the column can be used repeatedly in the preparation of radiochemically pure  $^{115\text{m}}\text{In}$ .

W. MIAKOWSKI

**5142. Concentration and colorimetric determination of titanium, aluminium, iron and magnesium in rock-salt.** Z. Marczenko and A. Stepien (Inst. Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 247-259.—Titanium, Al, Fe and Mg were separated from rock-salt soln. by pptn. with 8-hydroxyquinoline at pH 9.5 to 10.5. As a carrier the Ca present in the sample was used. The ppt. was filtered off and mineralised with  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ . Titanium was determined with chromotropic acid at pH 3. Iron was determined with 1:10-phenanthroline; various reducing agents were compared, the best results being obtained with ascorbic acid. Ascorbic acid was also used to eliminate interference by Fe in the determination of Al by means of aluminon. Magnesium was determined by Titan yellow, with poly(vinyl alcohol) as protective colloid. The methods were used for determination of metals over the range from 0.0001 to 0.005% with an accuracy of  $\pm 20\%$ .

L. SMAKOWSKI

**5143. Assay of sulphur and tantalum discs from criticality incident dosimeters.** W. R. Diggle and G. C. Jardine [U.K.A.E.A. (Development and Engineering Group), Dounreay Experimental Reactor Establishment]. U.K.A.E.A. Report DEG 156 (D), 1960, 13 pp.—Neutron-irradiated discs of Sulphur (1.8 g) are ignited on an aluminium counting tray (diam. 2 in.) and the  $^{32}\text{P}$  is measured by using a Geiger - Müller counter calibrated with a standard source of either  $^{32}\text{P}$  or  $^{90}\text{Sr}$ . Neutron-irradiated discs of tantalum (0.85 g) are counted with a  $\gamma$ -scintillation counter; this technique is preferred to the determination of the  $\beta$ -activity by means of Geiger - Müller counters or a  $\beta$ -scintillation counter. Results with gold foil (2.15 g) showed this to have a sensitivity 150 times that obtained with tantalum discs.

G. J. HUNTER

**5144. Acid chlorides of substituted succinic and glutaric acids as hydrolytic reagents for the determination of water.** R. Belcher, L. Ottendorfer and T. S. West (Univ., Edgbaston, Birmingham, England). *Talanta*, 1960, **4** (3), 166-173.—Improved reagents have been found for use in Lindner's method (*Ber.*, 1922, **55**, 2025) for determining water in gas streams by hydrolysis of acid chlorides. The  $\text{HCl}$  formed is determined titrimetrically. The compounds examined were—succinyl chloride (I),  $\alpha,\alpha$ -dimethyl- and  $\alpha,\alpha$ -diethyl-succinyl chlorides, glutaryl chloride,  $\beta,\beta$ -dimethyl- (II),  $\beta$ -methyl- $\beta$ -ethyl- (III) and  $\beta,\beta$ -diethyl-glutaryl chlorides, cyclohexyl-1:1-diacetyl chloride (IV) and naphthalyl chloride (V). I hydrolyses more rapidly than reagents used previously but gives high blank values and low results; II is the best reagent found so far, but is rather volatile, necessitating a cooling trap (ice - salt); III gives somewhat more variable results, but is much less volatile, and requires no cooling

trap. The other reagents are less satisfactory and **IV** and **V** are unsuitable. Full details of apparatus and procedure are given for the use of **III**. Results for four hydrated salts gave recoveries of 99.2 to 101.2% of the theoretical amounts of water of crystallisation.

R. M. S. HALL

**5145. Spectral method for the isotopic analysis of lithium.** F. F. Gavrilov. *Optics and Spectroscopy*, 1959, **7** (3), 185-187; English translation of *Optika i Spektroskopiya*, 1959, **7** (3), 285.—A spectrographic method for the determination of the relative abundance of the isotopes  $^6\text{Li}$  and  $^7\text{Li}$  is described. The line 6707.86 Å is used, the isotopic structure of the line being resolved by a grating spectrograph crossed with a Fabry-Perot étalon. The source is a hollow-cathode discharge device, the sample ( $\approx 3 \times 10^{-8}$  g) being in the form of a thin film deposited by electrolysis on to the polished face of the rod which forms the bottom of the hollow cathode. The relative abundance of  $^7\text{Li}$  to  $^6\text{Li}$  found by this method is  $12.2 \pm 0.3$ .

B. S. COOPER

**5146. Isotopic determination of lithium by neutron activation.** R. F. Coleman (U.K.A.E.A., Atomic Weapons Res. Estab., Aldermaston, Bucks., England). *Analyst*, 1960, **85**, 285-288.—The soln. of LiOH together with a standard soln. of known  $^6\text{Li}$  content is irradiated at a neutron flux of  $10^{12}$  neutrons per sq. cm per sec. for 30 min. In a weighed aliquot the activity of the  $^6\text{Li}$  produced by the reactions  $^6\text{Li}(n,\alpha)^3\text{He}$  and  $^6\text{Li}(n,\alpha)^3\text{H}$  is measured in a positron counter. The normality of the LiOH soln. is determined by micro-titration with N HCl. The activities of the sample and standard soln. are corrected by extrapolating back to the end of the irradiation. If the standard soln. (S g-atoms of  $^6\text{Li}$  per litre) has an activity of  $X_s$  at the end of the irradiation, and  $X_u$  is the activity of the unknown sample of normality  $N$ , the abundance of  $^6\text{Li}$  in the unknown sample is  $100SX_u/NX_s\%$ . With soln. containing  $<0.1$  g-atom of  $^6\text{Li}$  per litre, self-absorption of neutrons is negligible, and unless the LiOH is extremely impure, activities resulting from impurities do not affect the accuracy of the method. The error of the method determined by comparison with results obtained by mass spectrometry is  $\pm 2\%$ .

A. O. JONES

**5147. Synthetic inorganic ion-exchange materials. III. The separation of rubidium and caesium on zirconium phosphate.** C. B. Amphlett, L. A. McDonald, J. S. Burgess and J. C. Maynard (A.E.R.E., Harwell, England). *J. Inorg. Nuclear Chem.*, 1959, **10**, 69-73.—Experiments are described in which  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$  soln. were used to elute Rb and Cs (labelled with  $^{86}\text{Rb}$  and  $^{137}\text{Cs}$ ) from columns (2.5 cm length  $\times$  0.6 cm diam., and 13 cm length  $\times$  0.8 cm diam.) of zirconium phosphate, the  $\text{H}^+$  and  $\text{Na}^+$  forms of which were found to be superior to the  $\text{NH}_4^+$  form. A recovery of  $>97\%$  of pure Rb was obtained by elution with 0.1 M  $\text{NH}_4\text{NO}_3$ , and a recovery of  $>99\%$  of pure Cs by subsequent elution with conc.  $\text{NH}_4\text{NO}_3$  soln. that was 0.1 M with respect to  $\text{HNO}_3$ .

G. J. HUNTER

**5148. Rapid radiochemical determination of caesium-137.** Noboru Yamagata and Toshiko Yamagata (Coll. of Technol., Gunma Univ., Kiryu, Japan). *Analyst*, 1960, **85**, 282-285.—An amount of sample (food or biological material) containing  $\approx 0.1$  g of K is subjected to wet or dry ashing. To an acid soln. of the ash a CsCl carrier soln. (1.267% w/v) and a soln. of  $\text{FeCl}_3$  are added and the liquid

is scavenged by pptn. and removal of  $\text{Fe}(\text{OH})_3$ . To the cooled, stirred filtrate at pH 8 to 9 is added Na hexanitrodiphenylamine soln. and stirring is continued for 15 min. After 30 min. at  $0^\circ$  to  $5^\circ$  the ppt. of the hexanitrodiphenylamine salts of K and Cs is collected, dried and weighed (x g). The soln. of the ppt. in isobutyl methyl ketone is extracted with 2 N HCl. To the aq. soln. of the residue from evaporation of the extract,  $\text{H}_2\text{PtCl}_6$  is added, the ppt. of  $\text{Cs}_2\text{PtCl}_6$  is collected, dried and weighed (y g) and its activity is counted in a low-background  $\beta$ -counter, and corrected for self-absorption and scatter by reference to a calibration graph prepared from standard samples of  $^{137}\text{Cs}$  pptd. as  $\text{Cs}_2\text{PtCl}_6$  together with different amounts of carrier soln. If  $E$  ( $\mu\text{C}$ ) is the activity of the original sample and  $A$  ( $\mu\text{C}$ ) the corrected observed activity, then  $E = (0.0507A)/y$  and the amount of  $^{137}\text{Cs}$  per g of K in the original sample is  $E/(x - 0.0859)/0.0819$ .

A. O. JONES

**5149. Determination of copper.** A. L. Gershuns. USSR Pat. 126,295 (10.2.1960).—Copper is determined colorimetrically with 2:2'-bichinchonic acid (**I**), which with  $\text{Cu}^+$  forms an intense red-violet colour (absorption max. at 560 m $\mu$ ); the complex forms a stable soln. in water at pH 4 to 12. To construct a calibration curve, mix amounts of  $\text{Cu}(\text{NO}_3)_2$  soln. (10  $\mu\text{g}$  per ml) containing from 20 to 100  $\mu\text{g}$  of Cu with 5 drops of 10% hydroxyammonium chloride soln. and 2 ml of a 0.1% soln. of **I** in 2% KOH, dilute to 20 ml, adjust the pH to 6, make up to 25 ml, and measure the extinctions in a 1-cm cell with a green filter. Treat the sample soln. similarly; the accuracy is within  $\pm 1\%$ . Nickel, Co and Fe do not interfere; Cu can be determined in the presence of a 10,000-fold excess of Ni and a 60-fold excess of Fe at pH 6 in a soln. containing tartaric acid. **I** can detect 0.5  $\mu\text{g}$  of Cu in 10 ml and can determine 2 to 100  $\mu\text{g}$  of Cu per ml. The preparation of **I** is described.

C. D. KOPKIN

**5150. Conductimetric determination of copper.** G. B. Pasovskaya. *Izv. Akad. Nauk Turkmen. SSR*, 1959, (5), 73-74; *Ref. Zhur., Khim.*, 1960, (10), Abstr. No. 38,389.—A conductimetric determination of  $\text{Cu}^{2+}$  with thiosulphate in the presence of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and Sn is described. It is suitable for the determination of Cu in brass and bronze. Dissolve the alloy ( $\approx 0.5$  g) in a small quantity of  $\text{HNO}_3$  (1:1), evaporate the soln. on a water bath to a syrup, cool, dissolve the residue in  $\text{H}_2\text{O}$  and make up to 100 ml with  $\text{H}_2\text{O}$ . To an aliquot of the soln. ( $\approx 2$  mg of Cu) add a little solid  $\text{NH}_4\text{F}$  (to mask  $\text{Fe}^{3+}$ ), make up to  $\approx 25$  ml with  $\text{H}_2\text{O}$  and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  in a conductimetric apparatus. When approx. equal amounts of Cu and Zn are present, first titrate  $\text{Cu}^{2+}$  and then Zn. To determine Cu in bronze when the amount of Cu present is large and the amount of Zn small, add some  $\text{ZnSO}_4$  to the sample before titration; this facilitates the construction of a titration curve and reduces titration errors. It is possible to titrate 0.5 mg of Cu in 25 ml of soln. with an error of  $\approx 0.1\%$ .

K. R. C.

**5151. Analytical applications of complexones. IX. Absorptiometric and spectrophotometric micro-determination of copper with 1:2-diaminocyclohexane-NNN'-tetra-acetic acid.** F. Bermejo Martínez and R. Rey Mendoza. *An. Real Soc. Esp. Fis. Quim.*, B, 1959, **55**, 299-304.—The absorption of the chelate of Cu with 1:2-diaminocyclohexane-NNN'-tetra-acetic acid (**I**) follows Beer's law.



The absorption spectra of the chelate **I**-Cu<sup>2+</sup> at different pH values are studied; the spectra of two soln. of the chelate EDTA-Cu<sup>2+</sup> and **I**-Cu<sup>2+</sup> with the same concn. and pH are compared. The calibration curve is shown. The variation of extinction with pH and the chelate stability against time are determined. A theoretical interpretation of the different absorptions of the chelate at various pH values is given. The main differences are pointed out.

CHEM. ABSTR.

**5152. Methods for the analysis of copper alloys. Part 6. Tin (nickel coil reduction method).** British Standards Institution (2 Park Street, London, W.1). B.S.1748: Part 6: 1960. 5 pp.—The sample is dissolved in a mixture of HNO<sub>3</sub> and HCl. Tin is pptd. as hydroxide with ferric hydroxide as collector, then determined iodimetrically after reduction with nickel.

**Part 7. Silicon (photometric method).** B.S. 1748: Part 7: 1960. 7 pp.—Silicon is determined as molybdosilicate.

**Part 8. Phosphorus (photometric method).** B.S. 1748: Part 8: 1960. 7 pp.—Phosphorus is determined as molybdovanadophosphate. N. E.

**5153. Analysis of metallic samples by atomic absorption spectroscopy.** B. M. Gatehouse and A. Walsh (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Lab., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (5), 602-604.—Preliminary results are reported for the determination of 0.005 to 0.05% of Ag in copper by the method suggested by Russell and Walsh (*cf. Ibid.*, 1959, **15**, 883) which exploits the phenomenon of cathodic sputtering. Results of reproducibility tests with the apparatus illustrated, in which the flame is replaced by a sputtering chamber, show the standard deviation of the percentage of Ag to be  $\pm 0.0035$ .

E. G. CUMMINS

**5154. Application of ion exchangers to silver determination in low-copper ores.** W. Kemula, K. Brąjter, S. Cieślak and H. Lipińska-Kostrowicka (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 225-228.—In the method described, Ag was separated from other substances by pptn. as AgCl on an anion-exchange column and determined nephelometrically after elution with aq. NH<sub>3</sub>. The method was applied to the analysis of ores with a Ag content of 0.02% to 1.0%, with an average error of  $\approx 5\%$ .

L. SMAKOWSKI

**5155. Determination of small amounts of silver and mercury with thiofluorescein.** M. Wroński (Dept. Chem. Technol. Univ., Łódź). *Chem. Anal., Warsaw*, 1960, **5** (2), 289-291.—The sum of Ag<sup>+</sup> and Hg<sup>2+</sup> (0.005 to 0.2 mg) was determined by titration with a soln. of thiofluorescein (5 mg in 100 ml of 2% ethylamine) to a pale blue colour. A blank was also carried out. In a second sample Ag<sup>+</sup> were determined alone by adding to the slightly acid test soln. 0.3 ml of ethanol, 1 ml of 0.1 N EDTA (disodium salt) and 5 ml of aq. NH<sub>3</sub> and again titrating with thiofluorescein; Hg<sup>2+</sup> were determined by difference. The average error was 3%.

L. SMAKOWSKI

**5156. Determination of gold in sulphide ores by extraction.** G. O. Assarsson, K. Petersen and A. M. Askund (Geol. State Inst., Stockholm 50, Sweden). *Z. anal. Chem.*, 1960, **174** (3), 194-197 (in German).—The finely ground ore (50 g) is digested with 200 to 300 ml of HNO<sub>3</sub> (added in

70-ml portions). The insol. residue is dissolved in HCl (1:1) containing HNO<sub>3</sub> (10 to 20 drops) and Au is pptd., after addition of HgCl<sub>2</sub> (0.1 g), by means of 2 g of hydrazine sulphate and 5 g of sodium sulphide. The ppt. of Au and HgS is ignited, the residue is cupelled with pure lead, and the resulting gold bead is weighed on a micro-balance.

T. R. ANDREW

**5157. Polarography of beryllium.** K. Györfi (Inst. for Inorg. Chem., Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (2), 225-233 (in German).—When soln. of Be salts at pH 3.5 to 4.4 are polarographed with LiCl or tetramethylammonium iodide as basal electrolyte, two waves are observed, the height of the second wave being proportional to the concn. of Be<sup>2+</sup> over the range  $0.8 \times 10^{-3}$  to  $6 \times 10^{-3}$  M. The value of  $E_1$  is -1.85 V vs. the N.C.E. at pH 4.5 and in the presence of 0.1 M LiCl, moving to more negative values at lower pH. No shift of  $E_2$  occurs in the presence of complexing agents. No separation of Be from Al is possible, and Ba must be removed as BaSO<sub>4</sub>. Alkali metals interfere only when present in a large excess.

J. H. WATON

**5158. Analysis of beryllium and beryllium oxide. II. The determination of copper.** J. O. Hibbits, W. F. Davis and M. R. Menke (G.E.C., Aircraft Nuclear Propulsion Dept., Evendale, Ohio, U.S.A.). *Talanta*, 1960, **4** (2), 101-103 (in English).—Extraction of the complex of Cu and neocuproin (2:9-dimethyl-1:10-phenanthroline) (**I**) at pH 5 into isobutyl methyl ketone (**II**) permits the determination of Cu with an accuracy within  $\pm 5\%$  or  $\pm 2.5$   $\mu$ g, whichever is greater. The Be is kept in soln. by citric acid and of 68 elements studied only Au (5 mg) interferes, causing low results. *Procedure*—To a soln. of the sample ( $\approx 50$   $\mu$ g of Cu), prepared as previously described (*Ibid.*, 1960, **4**, 61) and containing 5 ml of HCl and 10 ml of H<sub>2</sub>SO<sub>4</sub>, add 50% (w/v) citric acid soln. (10 ml) and 10% hydroxyammonium chloride soln. (5 ml), dilute to 100 ml, and cool in ice. Adjust to pH 5.0  $\pm$  0.1 with 50% (w/v) NaOH soln. (at room temp.), add 0.1% ethanolic **I** soln. (10 ml) and set aside for 2 hr. Add **II** (10 ml), shake for 1 min., centrifuge and determine the extinction of the organic phase at 457 m $\mu$  in a 1-cm cell against **II**. Determine the Cu concn. from a calibration curve. A blank and a standard should be carried through the procedure.

**III. Determination of molybdenum.** J. O. Hibbits, W. F. Davis, M. R. Menke and S. Kalman. *Ibid.*, 1960, **4** (2), 104-107.—Extraction of the complex of Mo with SCN<sup>-</sup> into **II** permits the determination of Mo with an accuracy of  $\pm 4\%$  or  $\pm 3$   $\mu$ g, whichever is greater. Of 68 elements studied, only Rh, Pt, Re, V and Te (10 mg of each) interfere and only Re interferes seriously. *Procedure*—To a soln. of the sample ( $\approx 75$   $\mu$ g of Mo), prepared as previously described (*Ibid.*, 1960, **4**, 61), add citric acid (1 g) and a 0.1% soln. of Fe<sup>3+</sup> (1 ml). Then add HCl (5 ml) or H<sub>2</sub>SO<sub>4</sub> (10 ml) and water to 70 ml. Add satd. bromine water (2 ml), 25% KSCN soln. (10 ml) and 25% SnCl<sub>2</sub> soln. (5 ml), set aside for  $\leq 10$  min., add **II** (25 ml) and shake for 1.5 min. Separate and wash the organic phase with 2% oxalic acid soln. (35 ml) and then with 2.4 M HCl (35 ml). Keep the organic phase in a stoppered separating-funnel for 2 hr., centrifuge, and measure its extinction in a 2-cm cell at 500 m $\mu$  against **II**. Determine the Mo concn. from a calibration curve; a blank and a standard should be carried through the procedure.

J. P. STERN

**5159. Complexometric determination of calcium and magnesium with potentiometric end-point detection.** F. Štráfelda and J. Říhová (Dept. Spec. and Phys. Chem. Anal. Methods, Inst. Chem. Technol., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1444-1449 (in German).—As little as  $5 \times 10^{-4} M$   $Ca^{2+}$  in the presence of an excess of Mg can be determined potentiometrically with 0.1 M EDTA (disodium salt) as titrant and a mercury indicator electrode. Magnesium is pptd. as  $MgNH_4PO_4$  in ammoniacal soln., an excess of EDTA soln. is added and the excess is back-titrated potentiometrically with  $Ca^{2+}$  soln. (Přibil and Roubal, *Chem. Listy*, 1953, **47**, 189). The presence of  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $NO_3^-$ ,  $HCO_3^-$  and  $F^-$  ( $<0.1 M$ ) causes no interference; salts of heavy metals and alkaline-earth metals must be absent.

J. ZÝKA

**5160. Isolation of radiogenic calcium from mica for isotopic analysis.** V. I. Baranov and Yul-Vel Chen (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 163-165.—A method is described for isolating radiogenic Ca from lepidolite and muscovite giving a yield of more than 90% of the total Ca. *Procedure*—Decompose 1 g of the sample with 30 ml of freshly prepared pyrophosphoric acid in a silica beaker at a temp.  $>250^\circ$  for 5 min. Cool to room temp., add water to 150 to 250 ml, separate the  $SiO_2$  on a glass filter and pass the filtrate through a 12-mm column (20 g of cationite KU-2 in  $H^+$  form) at a rate of 2 ml per min. Wash the column with water to a neutral reaction, then elute the Al with aq.  $NH_3$  until there is no reaction with Alizarin red S and wash again to a neutral reaction. Then elute the K with 0.4 N HCl (400 ml) and the Ca and other remaining cations with N HCl (150 ml). After double pptn. of Fe and Mn with aq.  $NH_3$  in the presence of  $H_2O_2$ , the Ca in the filtrate is pptd. with oxalate.

A. BURWOOD-SMITH

**5161. The influence of vanadium on the flame emission of calcium.** Z. Řezáč and J. Dvořák (Res. Inst. for Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Z. anal. Chem.*, 1960, **174** (2), 96-104 (in German).—Quinquevalent V suppresses the flame emission of Ca; the reduction in intensity is proportional to the ratio of V to Ca for values up to about 1, at which ratio the intensity is about 45% of that in the absence of VV. Reduction by hydroxyammonium chloride to  $V^{IV}$  virtually eliminated the interference. It is suggested that the diminution in the calcium emission might be used for the indirect flame-photometric determination of VV. The effect of VV can also be eliminated by addition of La in a ratio of La to V of at least 4:1.

T. R. ANDREW

**5162. Effect of 8-hydroxyquinoline in flame spectrophotometric analysis.** Direct determination of strontium, calcium, potassium, sodium and lithium in the presence of interfering ions. Emission of aluminium in the presence of 8-hydroxyquinoline. J. Debras-Guedon and I. A. Voinovitch (Soc. Franç. Céram., Centre Nat. d'Études Céramique, Paris). *Chem. Anal., Warsaw*, 1960, **5** (2), 193-200 (in French).—It is shown that the addition of 8-hydroxyquinoline to the test soln. appreciably enhances the emission of Na, K, Li, Ca and Sr, to an extent proportional to its concn. A procedure is described whereby the interfering effects of Al, Fe, Ti, Mg,  $SO_4^{2-}$ ,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $PO_4^{3-}$  in the

simultaneous direct determination of the elements named are eliminated. The procedure is applicable to the analysis of silica - alumina refractories. The emission of Al in the oxy-acetylene or oxy-hydrogen flame is also sufficiently enhanced in the presence of 8-hydroxyquinoline to permit of the direct determination of Al in soln. of complex silicates.

L. SMAKOWSKI

**5163. Evaluation of zinc dust.** F. L. Hahn (Angel Urraza 718-303, Mexico 12). *Z. anal. Chem.*, 1960, **174** (4), 261-262 (in German).—Sources of error in the determination of the reducing power of zinc dust by reaction with  $Fe^{3+}$  are discussed. To avoid interference by traces of Cu, an excess of  $CuSO_4$  is added, which forms metallic copper. This then reacts with  $Fe^{3+}$  to give  $Fe^{2+}$ . *Procedure*—Weigh 160 mg of zinc into a dry flask, add rapidly 50 ml of 1.5%  $CuSO_4$  soln. and swirl for 1 min. Add 10 ml of  $M Fe_2(SO_4)_3$ , acidify with  $H_3PO_4$  and dilute to 200 ml. Titrate with 0.1 N  $KMnO_4$ . The blue colour due to  $Cu^{2+}$  does not interfere.

P. D. PARR-RICHARD

**5164. Determination of zinc in metallurgical materials by atomic-absorption spectrophotometry.** J. A. F. Gidley and J. T. Jones (I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1960, **85**, 249-256.—Four standard graphs are prepared from soln. containing 2.5 to 10 p.p.m. of Zn with a Hilger atomic-absorption attachment to a Uvispek spectrophotometer with photomultiplier recording, the extinction being expressed as the ratio of the recorded potential to that of water. A sample soln. containing 1 to 8 p.p.m. of Zn is suitable for measurement. Copper-based alloys containing no Sn or Si are dissolved in dil.  $HNO_3$ , those containing Sn in HBr - Br, the HBr being removed by evaporation with  $HNO_3$ , and those containing Si by fuming with  $HNO_3$ , HF and  $H_2SO_4$ . Zirconium and its alloys are dissolved in HF and fumed with  $HNO_3$  and  $H_2SO_4$ . Miscellaneous alloys are dissolved in any mixture of mineral acids, HF being used if Si is present, and any halogen acid used being completely removed by fuming with  $H_2SO_4$ . A preliminary fusion may be necessary. To prevent errors due to viscosity changes, the acid concn. in the final soln. should not exceed that corresponding to the dilution (1:19); otherwise a standard soln. with the same concn. of acid should be used as the comparison soln.

A. O. JONES

**5165. Determination of small amounts of cadmium in the presence of zinc by an indirect volumetric method.** Z. Drabent and W. Wawrzyczek (School of Agric., Olsztyn, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 201-205.—This method is based on the volumetric determination, by the Volhard method, of the  $SCN^-$  produced during the alkaline hydrolysis of Cd reineckate. The determination of Cd was possible even in the presence of a 90-fold excess of  $Zn^{2+}$ . Interference is caused by  $Ag^+$ ,  $Hg_2^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Tl^{2+}$ ,  $Cu^+$ ,  $Sn^{2+}$ ,  $Au^{3+}$  and  $Pd^{2+}$ .

L. SMAKOWSKI

**5166. Complexometric determination of mercuric and aluminium ions.** É. Bányai, É. B. Gere and L. Erdy (Inst. for Gen. Chem., Tech. Univ., Budapest, Hungary). *Talanta*, 1960, **4** (2), 133-140 (in English).—Diphenylcarbazide (I) or diphenylcarbazone (II) and 1:10-phenanthroline (III) form an indicator system suitable for the titration of  $Hg^{II}$  with EDTA (disodium salt) (IV) at pH 4 to 6,

and for the back-titration of Al with  $\text{Hg}(\text{NO}_3)_2$ . The coeff. of variation is  $\pm 0.24\%$ . Alternatively, xylenol orange may be used in the back-titration. Alkali and alkaline-earth metals,  $\text{Mg}^{2+}$  and  $\text{F}^-$  do not interfere, but  $\text{Cl}^-$  and  $\text{Mn}^{2+}$  do. *Procedure*.—To the sample (50 to 250 mg of Hg) add 20% hexamine soln. (5 to 10 ml), 0.2% ethanolic **III** soln. (1.5 ml) and 1% ethanolic **I** soln. (5 to 6 drops). Dilute to  $\approx 100$  ml and titrate with 0.05 *M* **IV** to the discharge of the violet colour. To determine Al (1 to 20 mg) add **IV** (20 to 200% excess), adjust with  $\text{HNO}_3$  until acid to phenolphthalein and dilute to  $\approx 100$  ml. Heat for 2 to 3 min., cool, add 20% hexamine soln. (10 ml), and titrate with  $\text{Hg}(\text{NO}_3)_2$  to a violet end-point, with 0.01 *M* **II** (0.2 ml) and 0.2% **III** soln. (0.5 ml) as indicator.

J. P. STERN

5167. Determination of mercury in brine and caustic soda by extractive titration with dithizone. W. Kemula, W. Brachaczek and A. Hulanicki (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 215-218.—The method is suitable for the determination of 1 to 15  $\mu\text{g}$  of Hg per 50 ml. It consists in the titration at pH 2 with a 0.02% soln. of dithizone in  $\text{CHCl}_3$ . There is no interference from Fe, Co, Ni, Zn, Bi, Pb, Mn or Cu, or from Ag (up to  $5 \times 10^{-3}$  *M*) if the chloride concn. exceeds 0.5 *M*. For the determination of Hg in technical caustic soda a preliminary distillation from 6 *N* HCl in the presence of  $\text{SnCl}_2$  is necessary, mercury vapour being absorbed in 0.1 *N*  $\text{KMnO}_4$ . The error was  $< 8.0\%$ .

L. SMAKOWSKI

5168. Determination of free boron in boron carbide, boron nitride and alloys based thereon. E. E. Kotlyar and T. N. Nazarchuk (Inst. of Metallo-ceramics and Special Alloys, Acad. Sci. UkrSSR, Kiev). *Zhur. Anal. Khim.*, 1960, **15** (2), 207-210.—The method is based on the oxidation of free boron with a mixture of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  whilst the boron combined in carbide or nitride is not attacked. *Procedure*.—Treat 0.1 to 1 g of  $\text{B}_4\text{C}$  or BN with a mixture of 45 to 75 ml of 5% aq.  $\text{H}_2\text{O}_2$  and 10 drops of  $\text{HNO}_3$ . Heat slowly and boil under reflux for 40 to 45 min. For large quantities of free boron boil for a longer time and add a further 3 to 5 ml of  $\text{H}_2\text{O}_2$  soln. Cool the soln. and filter off the insoluble  $\text{B}_4\text{C}$  and BN, washing several times with water and 2 or 3 times with 1% NaOH soln. Make the filtrate slightly acid and boil under reflux to remove  $\text{CO}_2$ . Cool and neutralise with 20% NaOH soln., add 1 to 2 drops of HCl (1:1), and neutralise with 0.1 *N* NaOH. To the soln. add 10 ml of a neutral 50% soln. of invert sugar and titrate with alkali to phenolphthalein. Simultaneously carry out a blank titration.

A. BURWOOD-SMITH

5169. Analysis of boron in borosilicate glasses by neutron transmission. P. R. Segatto (Corning Glass Works, New York). *J. Amer. Ceram. Soc.*, 1960, **43**, 278-281.—The sample is dissolved in 48% HF and the soln., contained in an annular polyethylene tubular cell, is placed in a block of paraffin wax (moderator) in which is also embedded a radium-beryllium neutron source. The detector, in the form of a tube containing enriched ( $^{10}\text{B}$ )  $\text{BF}_3$  at a pressure of 120 torr, is inserted in the annular test-cell. The attenuation by the test soln. is interpreted by means of a calibration curve prepared from soln. of  $\text{H}_3\text{BO}_3$  (the solubility range of which is extended by the addition of triethanolamine). The method is rapid (40 min.) and gives an accuracy

of  $\pm 1\%$  but requires 0.1 g of B in the test soln. (so that for a glass containing 10 to 15% of  $\text{B}_2\text{O}_3$  a sample of 4 g must be dissolved). Lithium oxide interferes, and must be determined by an independent method and a correction applied.

J. A. SUGDEN

5170. Colorimetric determination of boron in porcelain enamel frits. J. J. McIntosh and J. E. Cox (Mellon Inst., Pittsburgh, Pa.). *J. Amer. Ceram. Soc.*, 1960, **43** (3), 123-124.—Full details are given of a modified curcumin test. The colour is developed (without the normal step of evaporation and heating to 55°) by mixing the reagent soln. with an aliquot of the test soln. dissolved in glacial acetic acid and adding  $\text{H}_2\text{SO}_4$ . The method is rapid and its accuracy comparable with that of other methods.

J. A. SUGDEN

5171. Gravimetric determination of aluminium in bronze and brass. B. Alfonsi and M. Bussi (Auto-Avio, Fiat, Turin, Italy). *Anal. Chim. Acta*, 1960, **22** (4), 383-391.—Copper is separated by a preliminary pptn. with thioglycolic acid (**I**) which also serves to sequester certain other metals in the subsequent pptn. of Al with ammonium benzoate (**II**) (*cf.* Jewsbury and Osborn, *Brit. Abstr. C*, 1951, 195). The ppt. containing the Al is re-dissolved in  $\text{H}_2\text{SO}_4$  with the aid of  $\text{HNO}_3$  and  $\text{HClO}_4$ , the Al is again pptd. with **II** in the presence of **I**, the ppt. is ignited at 1200° and weighed as  $\text{Al}_2\text{O}_3$ . A number of results are given for synthetic and standard samples.

H. N. S.

5172. Indirect complexometric titration of aluminium. A study of the Wänninen-Ringbom method. F. Nydahl (Dept. of Anal. Chem., Univ. Uppsala, Sweden). *Talanta*, 1960, **4** (2), 141-146 (in English).—The Al-EDTA complex is inert in the indirect titration of Al with Zn as standard, and the method of Wänninen and Ringbom (*Anal. Abstr.*, 1955, **2**, 2360) is thus applicable over a wide range of conditions. For the titration of 0.2 to 2 millimoles and of 0.02 to 0.1 millimole of Al the mean recoveries are 99.93 and 100.04%, with coeff. of variation of 0.072% and 0.062%, respectively.

J. P. STERN

5173. The enhancement of the flame spectrum of aluminium by fluoride ions. K. Konopicky and W. Schmidt (Forsch.-Inst. der Feuerfest-Ind., Bonn, Germany). *Z. anal. Chem.*, 1960, **174** (4), 262-268 (in German).—The addition of HF and butanol to aluminium soln. results in an enhanced emission, particularly at 484  $\text{m}\mu$ . The limits of detectability for an aluminium soln. alone, with butanol, with HF, and with butanol and HF were 60, 5, 2 and 1 mg of  $\text{Al}_2\text{O}_3$  per 100 ml, respectively. The enhancement is due to the formation of  $\text{AlF}_3$ , and excess of HF over the stoichiometric amount causes no further increase. Nitric acid has no effect, and  $\text{HClO}_4$  or oxalic acid very little, but  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  reduce the emission seriously. Of the cations Na, K, Ca, Mg, Fe and Ti, present in the proportions found in clays, only Ca caused a slight reduction, which was corrected by adding Ca to the standard soln. Fluoride has little effect on the emission of other elements except for Ca (large reduction) and B (increased emission).

P. D. PARR-RICHARD

5174. Influence of the form of combination of an element [aluminium] on its determination by emission spectrum analysis. P. Dickens and A. Bähr (Chem. Lab., Mannesmann Hüttenwerke

A.-G., Duisberg-Huckingen). *Arch. Eisenhüttenw.*, 1960, **31** (3), 135-143.—Electrodes prepared from Al-Cu alloy,  $Al_2O_3$  with Cu, and AlN with Cu were compared. It was found that the actual form or state of combination of the Al does not affect the results, provided that arcing is continued until the ratio of the intensities of the Al emission band to that of the Cu emission band attains equilibrium before readings are taken. When this condition is fulfilled a calibration curve obtained with metallic aluminium can be used for establishing the content of Al from the emission spectrum of any aluminium compound. H. L. WHITEHEAD

5175. The minimum ignition temperature of aluminium oxide precipitates. O. I. Milner and L. Gordon (Res. Dept., Socony Mobil Oil Inc., Paulsboro, N.J., U.S.A.). *Talanta*, 1960, **4** (2), 115-119 (in English).—The safe min. temp. for the ignition, by conventional techniques, of the ppt. of hydrated  $Al_2O_3$ , basic  $Al_2(SO_4)_3$  or basic Al succinate to constant wt. is  $1200^\circ$ . J. P. STERN

5176. Determination of the hydrogen content of aluminium alloys with the "Telegas" apparatus. H. Plate (Verein Dtsch. Giessereifachleute, Neckarsulm, Württemberg). *Giesserei*, 1960, **47** (8), 208-210.—The operation of the "Telegas" apparatus (Ransley *et al.*, *J. Inst. Metals*, 1957-58, **86**, 212), in which a small vol. of N is circulated through the molten alloy and the H content of the equilibrated gas mixture is determined by thermal conductivity, was tested by determining the H content of aluminium alloys. The results were reproducible and showed good agreement with values obtained by other methods. Comments are made on the construction of the apparatus. J. H. WATON

5177. Simultaneous determination of copper and iron in high-purity aluminium using the K 1000 cathode-ray polarograph. J. Hetman (Southern Instruments Ltd., Camberley, England). *Anal. Chim. Acta*, 1960, **22** (4), 394-398.—The method is suitable for the analysis of high-purity (>99.99%) aluminium. The sample (0.5 g) is dissolved in 5 ml of 20% NaOH soln., 2 ml of M sucrose is added and the soln. is diluted to 10 ml. The Cu wave is observed on a start potential of  $-0.1$  V and a scale factor of 0.04 with direct current, and the Fe on a start potential of  $-0.6$  V and a scale factor of 0.004 with derivative current. If Mn is present, EDTA (2%) must be added. Results quoted cover the ranges 3 to 30 p.p.m. of Cu and 5 to 15 p.p.m. of Fe. Lead can also be determined simultaneously. H. N. S.

5178. Detection of gallium in the products of aluminium production. V. K. Kuznetsova and N. A. Tananaev (Acad. Sci., USSR, Sverdlovsk). *Zhur. Anal. Khim.*, 1960, **15** (2), 240-241.—Gallium is isolated by pptn. on titanium hydroxide and detected as an alizarin lake which is extracted with ethyl ether from ammoniacal oxalate buffer. To the test soln. is added  $TiCl_4$  soln. and then aq.  $NH_3$  dropwise until a ppt. appears. A little  $(NH_4)_2SO_4$  is added to coagulate the ppt., which is filtered off and treated with 3 to 4 ml of 10% NaOH soln. and some solid ammonium oxalate to pH 8 to 10. The mixture is shaken for 1 to 2 min. and a few drops of ethanolic alizarin soln. are added, together with 1 to 2 ml of ethyl ether. After further agitation, a slightly red layer of org. solvent containing the Ga separates. A. BURWOOD-SMITH

5179. Utilisation of ternary and ion-association complexes in chemical analysis. II. Polarographic determination of indium. M. Kopanica and R. Pribil (Chem. Inst., Czech. Acad. Sci., Prague). *Talanta*, 1960, **4** (3), 158-165 (in English).—Indium is separated from Cd, Zn,  $Mn^{II}$ ,  $Cu^{II}$ ,  $Ni^{II}$ ,  $Fe^{II}$ , Co and  $Mo^{VI}$  at pH 3 by forming the 1:10-phenanthroline-thiocyanate complexes in the presence of EDTA (disodium salt); In is retained in solution as an EDTA complex, and the other complexes can be dispersed into butanol and separated (no true solvent was found). The excess of 1:10-phenanthroline must also be removed by the addition of SCN<sup>-</sup> and dispersal of the resulting complex into butanol. The In-EDTA complex is then decomposed by acidifying to 3 M in HCl and determined polarographically after removal of O ( $E_1 = -0.64$  V vs. the S.C.E.). This value is constant for 2 hr., then SCN<sup>-</sup> are reduced to  $H_2S$  and the potential becomes more negative. For 0.05 to 0.5% of In in cadmium the error is  $< \pm 5\%$ ; for 0.5 to 5% the error is  $\pm 2\%$ . The sample used should contain at least 0.8 mg of In. R. M. S. HALL

5180. Rapid methods for spectrographic analysis of rare elements. I. Analysis of complex mixtures of rare earths. V. A. Korneev. *Zhur. Anal. Khim.*, 1960, **15** (2), 170-174.—A rapid method for the complete analysis of complex mixtures of rare earths is based on the use of homologous pairs in combination with step-by-step attenuation of the spectrum. The method permits the simultaneous determination of all the individual rare-earth elements in the range of concn. 0.1 to 100% with an accuracy of  $\pm 10$  to 20%. The method is 8 to 10 times as rapid as other spectrographic methods. A. BURWOOD-SMITH

5181. Spectrochemical determination of lanthanum and scandium in standard granite G1 by the method of addition. S. Held (Israel Atomic Energy Commission). *Spectrochim. Acta*, 1960, **16** (5), 588-594.—Confidence limits of the unknown concn. obtained with two sets of two additions and the limits obtained with a single addition were found to be of the same order of magnitude. It is therefore concluded that a single addition may often be sufficient for relatively rapid semi-quantitative determinations in geological work. Discrepancies between the results of the determinations of La and Sc in standard granite G1 (U.S. Geol. Survey) given here and quoted elsewhere are discussed. E. G. CUMMINS

5182. Flame spectra of scandium, yttrium and rare-earth elements. T. C. Rains, H. P. House and O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (4), 315-327.—Aqueous soln. of salts of Sc, Y and the rare-earth elements (except Ce and Pm) are extracted with a soln. of 2-thenoyltrifluoroacetone (I) in 4-methyl-2-pentanone and the extracts are introduced into the oxy-hydrogen flame of a recording flame spectrophotometer. Complex formation with I greatly enhances the emissivity of the elements. The wavelength and relative spectral intensity are tabulated for each line and band. Tabulated data and notes on mutual interference are also provided. H. N. S.

5183. Determination of carbon disulphide by chloramine T. V. R. Satyanarayana Rao and A. R. Vasudeva Murthy (Dept. of Inorg. and Phys. Chem., Indian Inst. of Sci., Bangalore). *Talanta*, 1960, **4** (3), 206-209.—Carbon disulphide is converted into K ethylxanthate by reaction with 10%



ethanolic KOH soln.; the xanthate is then quant. oxidised to  $\text{H}_2\text{SO}_4$  by chloramine T, the excess of reagent being determined iodimetrically after 30 min. No blank determination is necessary if fresh ethanolic KOH soln. is used. Fourteen equivalents of chloramine T are required per mole of  $\text{CS}_2$ .

R. M. S. HALL

**5184. Determination of carbon disulphide by means of the sodium azide-iodine reaction.** Z. Kurzawa and Z. Meybaum (Inst. Technol., Poznań, Poland). *Chem. Anal.*, Warsaw, 1960, 5 (2), 333-334.—Carbon disulphide catalyses the reaction  $2\text{NaN}_3 + \text{I}_2 \rightarrow 2\text{NaI} + 3\text{N}_2$ , and a method for the determination of  $\text{CS}_2$  (0.05 to 1 mg) in aq. soln. based on the consumption of iodine is described. The slow reaction induced by  $\text{CS}_2$  and the rapid one induced by  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SCN}^-$  and  $\text{SH}^-$  makes it possible to determine  $\text{CS}_2$  in the presence of these substances (up to 0.06 mg of bivalent S). The accuracy is  $\pm 5\%$ .

L. SMAKOWSKI

**5185. Dithizone method for determining small concentrations of cyanides.** A. D. Miller and M. I. Aranovich. *Zavod. Lab.*, 1960, 26 (4), 426-429.—At a pH of <8.0, simple and complex cyanides of Cu and Zn, but not ferrocyanides and ferricyanides, destroy the dithizone complex of Ag. When Cu, Zn and Pb are absent or, if present, complexed with EDTA, the weakening of the colour is a measure of the amount of  $\text{CN}^-$  present. To determine  $\text{CN}^-$  in water, the sample is first clarified and freed from organic material by treating it with HCl (1:9) to give a pH of between 4.5 and 5 and shaking it with  $\text{CCl}_4$  (5-ml portions). A vol. of the treated sample, containing between 2 and 20  $\mu\text{g}$  of  $\text{CN}^-$ , is mixed with 5 ml of 0.1 N EDTA (disodium salt) and treated with 0.1 N NaOH until it gives a blue colour with bromothymol blue. A soln. of  $\text{Na}_2\text{B}_4\text{O}_7$  (pH 9.24) (5 ml) and 2 ml of a soln. of Ag-dithizone complex in  $\text{CCl}_4$ , containing  $\approx 10 \mu\text{g}$  of Ag per ml, are added, the mixture is shaken for 3 min., and the extinction of the  $\text{CCl}_4$  layer is measured. The content of  $\text{CN}^-$  is determined from a calibration curve. The Ag-dithizone soln. is prepared by shaking a suitable vol. of a soln. of dithizone in  $\text{CCl}_4$ , containing dithizone equivalent to  $\approx 10 \mu\text{g}$  of Ag per ml, with excess of an aq. soln., 0.5 N in  $\text{H}_2\text{SO}_4$ , of Ag containing between 10 and 30  $\mu\text{g}$  of Ag per ml. The  $\text{CCl}_4$  soln. is then washed with water to remove excess of Ag. With samples containing  $\text{S}^{2-}$  or free Cl, the soln. is treated with  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{SO}_3$  or  $\text{Na}_2\text{S}_2\text{O}_3$  before the addition of EDTA.

G. S. SMITH

**5186. Process for determining cyanide concentrations in solution.** Deutsche Gold-und-Silber-Scheideanstalt vormals Roessler. Brit. Pat. 843,028; date appl. 7.11.57. Germany, date appl. 9.11.56 and 26.4.57.—The concn. of  $\text{CN}^-$  in aq. soln. is determined potentiometrically by means of a metal measuring electrode and a reference electrode serving for the potential discharge. An auxiliary current (5 to 20  $\mu\text{A}$  per sq. dm) is passed between the measuring electrode and an auxiliary electrode. The metal used for the measuring and auxiliary electrodes is one that is capable of forming complex cyanides and is at least as noble as the noblest metal in the solution to be measured (e.g., copper, silver, gold or platinum, but excluding zinc and iron).

J. M. JACOBS

**5187. Detection of tin in tungsten minerals.** P. G. Jeffery (Geol. Survey, Entebbe, Uganda). *Rec. Geol. Surv. Uganda*, 1955-1956 (Publ. 1959), 43-44.—Tin can be identified by the red colour it

produces with toluene-3:4-dithiol if 5 g of citric acid is added to prevent the pptn. of the tungsten complex. Interference of Mo is avoided by extraction of the molybdenum complex with light petroleum. A distinct colour is given with 0.001% of Sn.

CHEM. ABSTR.

**5188. Polarographic determination of small amounts of tin and lead in zirconium and its alloys.** R. T. Clark (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1960, 85, 245-249.—The soln. of the sample in dil.  $\text{H}_2\text{SO}_4$  and HF is evaporated to fuming with  $\text{HNO}_3$ . To the aq. soln. of the residue are added  $M$  HCl and  $4M$   $\text{NH}_4\text{Cl}$  and, if the sample contains  $> \approx 200$  p.p.m. of Cu or 500 p.p.m. of Mo (or both), 2 ml of 2%  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. An aliquot of the diluted soln. is transferred to a polarograph cell, N or Ar is bubbled through to remove O, the polarogram (starting potential  $-0.2$  V) is recorded with a cathode-ray polarograph and the wave height is measured at  $-0.42$  V. The remainder of the electrolyte is treated with 1 ml of 25%  $\text{BaCl}_2$  soln. and the polarogram is recorded. The wave height at  $-0.42$  V due to Sn alone is measured, a positive correction of 5% is made and the corrected wave height is deducted from that of the Sn and Pb together. A reagent blank and a control soln. ( $\approx 50$  p.p.m. of Sn and Pb) are used. The standard deviation is  $\approx 2$  p.p.m. for both Sn and Pb at the 40 p.p.m. level.

A. O. JONES

**5189. Separation of titanium from tungsten by ion-exchange chromatography.** D. I. Ryabchikov and V. E. Bukhtiarov (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1960, 15 (2), 242.—Titanium and W are transformed into complex ions with opposite charges in an ammoniacal medium (pH 5) and in the presence of  $\text{H}_2\text{O}_2$ . *Procedure*—To 50 ml of slightly acid test soln. add 10%  $\text{H}_2\text{O}_2$  soln. (50 ml) and aq.  $\text{NH}_3$  soln. to pH 5. Pass the soln. through a column (300 mm long  $\times$  15 mm diam.) of cationite SBS ( $\text{H}^+$  form) at a rate of 3 to 4 ml per min. Elute the adsorbed Ti ions with 10%  $\text{H}_2\text{SO}_4$  soln. (250 ml at 10 ml per min.). Determine the Ti combined with  $\text{H}_2\text{O}_2$  by colorimetric titration. Heat the W-containing filtrate with  $\text{H}_2\text{SO}_4$  to decompose  $\text{H}_2\text{O}_2$  and determine W by titrating with  $\text{TiCl}_3$  with thiocyanate as indicator.

A. BURWOOD-SMITH

**5190. Chromatographic separation of titanium from niobium and tantalum.** V. I. Bogdanova. *Mater. Geol. Rudn. Mestorozhd., Petrogr., Miner., Geokhim., M., Akad. Nauk SSSR*, 1959, 224-232; *Ref. Zhur., Khim.*, 1960, (10), Abstr. No. 38,376.—Niobium, Ta and Ti are separated on cellulose by means of partition chromatography. Dissolve the mineral (0.1 to 0.3 g) in a mixture of HF and  $\text{HNO}_3$ , evaporate almost to dryness, add 25% HF soln. (6 ml),  $\text{NH}_4\text{F}$  (3 to 4 g) and radioactive Nb. Pour the soln. on to the cellulose in a polyethylene tube and pass ethyl methyl ketone (I) (400 ml), containing 15% HF, through it. Titanium and most of the other elements remain on the column while Nb and Ta are eluted. Evaporate the I, calcine the residue, fuse with  $\text{K}_2\text{S}_2\text{O}_8$ , treat with 1% tannin soln. and 5% HCl, and complete the determination of Ta and Nb gravimetrically or photometrically. Calculate the Nb retained on the column by determining the activity of the cellulose and make a correction to the amount of Nb found in the eluate. To separate Nb and Ta, different solvents are used for elution: pure I elutes almost all

the Ta, and I containing HF elutes Nb and the remaining Ta; the minimum column length is 30 cm and the solvent is passed through at  $> 10$  ml per min.

K. R. C.

**5191. Determination of some impurities in titanium dioxide.** F. Plesnivý (Res. Inst. Vacuum Electrochem., Prague). *Skřáf a Keram.*, 1960, **10** (3), 77-80. —Detailed procedures are given. After dissolution of the sample in  $H_2SO_4$ -HF, Fe is separated from Ti by pptn. with  $H_2S$  from tartrate soln. and determined colorimetrically with  $SCN^-$ . Alkali metals are determined polarographically in tetramethylammonium hydroxide soln. after extraction of another portion of sample with  $SO_2$  soln. and destruction of organic matter with  $HClO_4$ . Sulphates are extracted in a Soxhlet apparatus and determined by amperometric titration with 0.1 M  $Pb(NO_3)_2$  in 50% ethanol medium. Barium (in  $BaTiO_3$ ) is extracted with N acetic acid and determined polarographically in LiOH soln.; the same extractant is recommended for the determination of Pb in  $PbTiO_3$ , polarography being carried out in acetic acid soln. For Ca (in  $CaTiO_3$ ) the extraction is with N acetic acid, and the Ca is pptd. as the picrolonate and determined colorimetrically after treatment with alkaline bromine water. Procedures are also given for the determination of Pb and Ca in barium titanate.

J. ZÝKA

**5192. The application of infra-red spectroscopy to the analysis of titanium tetrachloride.** D. T. Tsekhovolskaya, T. A. Zavaritskaya, G. S. Denisov and V. M. Chulanovskii (Phys. Inst., Univ., Leningrad, U.S.S.R.). *Spectrochim. Acta*, 1960, **16** (5), 547-550 (in English).—Examination of technical  $TiCl_4$  samples, carried out on single-beam spectrometers with LiF prisms for the range 1800 to 3600  $cm^{-1}$  and NaCl prisms for the range 700 to 1850  $cm^{-1}$ , has revealed a large number of absorption bands belonging to organic and inorganic impurities. The spectra of standard soln. in  $TiCl_4$  of these substances, which include  $HCl$ ,  $TiOCl_2$ ,  $VOCl_3$ ,  $COCl_2$ ,  $C_2Cl_6$ ,  $CHCl_3$ ,  $CCl_4$ ,  $CH_2Cl_2$ ,  $CH_3COCl$  and  $CO_2$ , demonstrate obedience to the Beer-Lambert law, and a table shows the sensitivity of an impurity determination when using any band assigned to one of these.

E. G. CUMMINS

**5193. Volumetric determination of zirconium. II. Chromate method.** A. Schneer and H. Hartmann (Inst. for Gen. and Inorg. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (2), 139-151 (in German).—After the separation of Zr with mandelic acid (cf. *Anal. Abstr.*, 1959, **6**, 3444), the ppt. is dissolved in conc.  $H_2SO_4$ . Excess of  $Na_2Cr_2O_7$  in conc.  $H_2SO_4$  is added and the soln. is diluted to contain 75 to 80% of  $H_2SO_4$ . Oxidation of the mandelic acid is brought about by heating the soln. on an air bath at 115° for 20 min. The residual  $Na_2Cr_2O_7$  ( $\approx 0.06$  N) is back-titrated with standard  $FeSO_4$  soln. (0.1 or 0.3 N), with ferroin as indicator; 1 ml of 0.1 N  $Na_2Cr_2O_7$  = 0.447 mg of mandelic acid or 67.07  $\mu g$  of Zr. A correction of +2% is applied to compensate for the negative error obtained in the oxidation of mandelic acid when 0.5 to 5 mg of Zr is being determined; the results are then accurate to 1% and are reproducible. For smaller amounts of Zr (e.g.,  $\approx 100$   $\mu g$ ), the error increases up to  $\pm 10\%$ . No previous separation of B, Si, Ta, Nb, W, Sn or Ti is necessary. The method has been successfully applied to the analysis of rocks containing 0.01 to 0.1% of Zr. For the

determination of Zr in "red mud," 1 to 2 g of sample is used instead of the 5 g as previously described (*loc. cit.*).

J. H. WATON

**5194. Colorimetric determination of zirconium by means of arsenazo III.** V. G. Goryushina and E. V. Romanova. *Zavod. Lab.*, 1960, **26** (4), 415-418.—A soln., 2 N in HCl, containing from 5 to 30  $\mu g$  of Zr, is treated with 3 ml of 1% gelatin soln. and 1 ml of 0.1% aq. arsenazo III soln. [2:7-di-(o-arsenophenylazo)-1:8-dihydroxy naphthalene-3:6-disulphonic acid], and diluted to 50 ml with 2 N HCl. The extinction of the blue soln. is measured with a red filter. The following metals, in the indicated amounts, do not interfere: Be (10 mg), Ni (10 mg),  $Cu^{II}$  (3 mg),  $Cu^I$  (5 mg), Cr (5 mg), Al (100 mg),  $Fe^{III}$  (5 mg),  $Fe^{II}$  (15 mg), rare-earth metals (5 mg),  $Ti^{IV}$  (10 mg),  $Sn^{IV}$  (20 mg) and Nb (5 mg). Interference is caused by Th and U, and also by  $F^-$ ,  $PO_4^{3-}$  and oxalate, but not by  $NO_3^-$ ,  $SO_4^{2-}$  (100 mg) or tartrate (50 mg). The method is applied to the determination of Zr in various mineral raw materials.

G. S. SMITH

**5195. Determination of zirconium, boron and carbon in zirconium diboride.** L. Kábrt and Z. Marek (V.Ú.P.M., Vestec u Praha, Czechoslovakia). *Hutn. Listy*, 1960, **15** (4), 297-299.—*Procedure for zirconium*—Dissolve the sample (0.2 to 0.5 g) by heating in  $H_2SO_4$  (1:1) (20 ml), add a few drops of  $HNO_3$  and remove oxides of N. Filter off the dark insoluble residue eventually formed after dilution with  $H_2O$ . Dilute the filtrate to 250 ml. To an aliquot add 0.05 M EDTA (disodium salt), tartaric acid soln. (20%) (20 ml) and ammonium acetate soln. (20%) (2 ml), neutralise with aq.  $NH_3$  to pH 1.5 (tropaeolin OO as indicator), boil gently for 10 min., cool and titrate with 0.05 M  $Bi(NO_3)_3$  (0.1% xylene orange as indicator) till the soln. is red. *Boron*—Fuse the sample (0.2 to 0.5 g) with a tenfold excess of  $KNaCO_3$ ; dissolve the melt in  $H_2O$  (50 to 70 ml), transfer with the undissolved residue to a 250-ml flask, dilute with  $H_2O$  to the mark, cool, and filter; neutralise to methyl orange with HCl, add 0.2 N HCl (1 ml), remove  $CO_2$  by boiling for 10 min. under reflux, cool, and neutralise with 0.2 N NaOH till the soln. is yellow; add mannitol (4 g) and titrate with 0.2 N NaOH to phenolphthalein. *Carbon*—Mix the sample (0.3 to 1 g) with  $CuO$  (wire) and ignite in a stream of O at 900° to 1000°. Determine the  $CO_2$  volumetrically.

J. ZÝKA

**5196. The analysis of zirconium-tungsten, hafnium-tungsten and thorium-tungsten alloys and of thoriated and zirconized tungsten by means of EDTA titration.** E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte/Tirol). *Planseeber. Pulvermet.*, 1960, **8** (1), 37-39.—After dissolution of the sample (5 g) in HF- $HNO_3$  (1:1), KOH is used to precipitate Zr, Hf and Th. Thorium-containing samples need an additional  $K_2S_2O_8$  fusion for dissolution. The ppt. is dissolved in  $HNO_3$  (1:1), and the filtered soln. is made up to 200 ml. An aliquot (50 ml) is treated with an excess of EDTA (disodium salt) soln., the pH is adjusted to 2 to 3 with dil. aq.  $NH_3$  and the excess of EDTA is back-titrated with standard W or Th soln.

G. P. MITCHELL

**5197. Spectrophotometric determination of zirconium in uranium alloys of the fission elements.** R. P. Larsen, L. E. Ross and G. Kesser (Chem. Engng Div., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Talanta*, 1960, **4** (2), 108-114 (in English).—



The Zr (0.01 to 1%) in uranium containing Mo (2.5%), Ru (1.5%), Rh (0.5%), Pd (0.3%), Nb and Te is separated by co-pptn. with  $\text{BaSiF}_6$  and determined spectrophotometrically as the complex with Alizarin red S. The method reveals small changes in alloy composition (within a factor of 2 at the 0.01% level) and is suitable for the control of the Zr content of the re-used fuel of a breeder reactor. Positive errors are caused by Rh. *Procedure*—Dissolve the sample in  $\text{HCl}$ - $\text{HNO}_3$ - $\text{HF}$  in a quartz flask (Larsen, *Anal. Chem.*, 1959, **31**, 545), dilute, and take an aliquot (70 to 300  $\mu\text{g}$  of Zr). Dilute with water to 3 ml, neutralise with 15 N aq.  $\text{NH}_3$  until a ppt. forms, and dissolve the ppt. by adding 16 N  $\text{HNO}_3$  dropwise. Add 16 N  $\text{HNO}_3$  (0.5 ml), 27 N  $\text{HF}$  (1.0 ml) and 0.2 M  $\text{H}_2\text{SiF}_6$  (4 drops), stir, heat on a water bath at  $90^\circ$  to  $100^\circ$  for 1 min. and add satd.  $\text{Ba}(\text{NO}_3)_2$  soln. (1.5 ml). Centrifuge and slurry the ppt. with water (2 ml plus two 1-ml washes). Add 70%  $\text{HClO}_4$  and evaporate to dryness. Add 3 N  $\text{HF}$  (3 drops), water (1 ml) and 70%  $\text{HClO}_4$  (2 ml) and heat to fuming. Re-fume twice after cooling and adding water (1 ml). Then make up the  $\text{HClO}_4$  to 2-30 g. add water (5 ml), warm gently, add 0.2% Alizarin red S in 0.1 M  $\text{HClO}_4$  (1 ml) and dilute to 25 ml. Measure the extinction at 520  $\mu\text{m}$  in a 1-cm cell after 18 hr. against a reagent blank. Read the Zr content from a calibration curve. J. P. STERN

#### 5198. Organic azo dyes in quantitative analysis.

**I. Complexometric titration of thorium.** M. R. Zaki and K. Shakir (Atomic Energy Estab., Cairo, Egypt). *Z. anal. Chem.*, 1960, **174** (4), 274-278 (in English).—Indicators for the titration of Th with EDTA are reviewed. By using the dye Eliamina Blue FFL (C.I. Direct Blue 71) (I),  $<20 \mu\text{g}$  of Th per 10 ml can be titrated with an error of  $\pm 2\%$ . The effects of pH, concn. and of foreign cations are discussed. A 10-fold excess of  $\text{Sb}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{As}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{U}^{6+}$ ,  $\text{Ca}$ ,  $\text{Pb}$ ,  $\text{Cd}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Co}$ ,  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  is permissible, but  $\text{Fe}^{3+}$ ,  $\text{Zr}$ ,  $\text{Cu}$ ,  $\text{Ni}$  and  $\text{Al}$  interfere. *Procedure*—After dissolution of the sample and removal of interfering cations, evaporate the soln. to dryness and dissolve the residue in 0.01 N  $\text{HNO}_3$  to make a known vol. Dilute 1 ml (containing  $>20 \text{ mg}$  of Th) with  $\text{H}_2\text{O}$  (10 ml); the final pH should be between 2.5 and 3.5. Add 1 to 5 ml of a 0.01% soln. of I, warm to  $70^\circ$  and titrate with EDTA. P. D. PARR-RICHARD

**5199. Photometric determination of thorium in monazites with arsenazo II reagent.** V. I. Kuznetsov and S. B. Savvin (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 175-179.—Thorium is determined in monazites without separation from impurities. No interference is caused by phosphates (up to 30% of  $\text{P}_2\text{O}_5$ ), Zr, Ti, Mo, V, W (up to 0.5%), rare-earth metals and other elements. A determination takes 25 to 30 min. and errors are  $>5\%$ . *Procedure*—Place 10 to 200 mg of finely divided monazite, with a Th content of  $>0.5\%$ , in a silica test-tube and fuse with 2 g of  $\text{K}_2\text{S}_2\text{O}_7$ . Heat slowly for a few minutes and then at a dull red heat. Dissolve the melt in  $\text{HCl}$  (1:1) (40 ml) and dilute with water to 100 ml. Filter and transfer a 2.5-ml aliquot to a 25-ml flask. For monazites with Th contents  $>15\%$  take a smaller aliquot. In this case also add 2.5 ml of 2%  $\text{K}_2\text{S}_2\text{O}_7$  soln. in  $\text{HCl}$  (1:5). Add 10 to 20 mg of ascorbic acid if Fe is present, 0.5%  $\text{NaH}_2\text{PO}_4$  soln. (2 ml), 0.1% arsenazo II soln. (5 ml) and water to 25 ml. Mix

for  $<5$  min. and measure the extinction at 600  $\mu\text{m}$ . Refer the results to a calibration curve.

A. BURWOOD-SMITH

**5200. Photometric determination of thorium in minerals by means of arsenazo III.** S. B. Savvin and V. V. Bagreev (Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (4), 412-415.—The separated and washed insoluble matter, obtained after repeated treatment of the sample (0.05 to 0.5 g) with  $\text{HF}$  soln. followed by evaporation and addition of water, is treated with 4 ml of conc.  $\text{HCl}$  and the soln. is evaporated to dryness. The residue is treated with 2 ml of  $\text{HClO}_4$  and 1 ml of  $\text{HCl}$ , and 2 to 5 ml of water, and the soln. is evaporated to fuming. The evaporation is repeated after addition of 1 ml of  $\text{HCl}$  and 2 to 5 ml of water. The residue is dissolved in 4 ml of  $\text{HCl}$  (1:1) and 5 to 7 ml of water, and the soln. is diluted to 25 ml. A 10-ml portion of this soln. is treated with ascorbic acid if Fe is present and then with 10 ml of a 4% soln. of oxalic acid in  $\text{HCl}$  (1:1) and 0.5 ml of a 1% aq. soln. of arsenazo III (2:7-di-(*o*-arsonophenylazo)-1:8-dihydroxy-naphthalene-3:6-disulphonic acid), and diluted to 25 ml. The extinction is measured at 665  $\mu\text{m}$ . With contents of Th  $<0.001\%$ , the residue obtained after the evaporations is dissolved in 1.6 ml of  $\text{HCl}$  (1:1) and 5 ml of water, and the whole of the soln. is used. The method is suitable for determining contents of Th  $<0.0001\%$ . G. S. SMITH

#### 5201. Use of organic reagents in inorganic analysis.

**XIII. Determination of thorium and zirconium with aryloxy fatty acids.** Sachindra Kumar Datta (Victoria (Government) College, Coochbehar, India). *Z. anal. Chem.*, 1960, **174** (2), 109-118 (in English).—Fourteen aryloxy fatty acids have been studied as pptn. reagents for Zr and Th. Within the pH range 3 to 4.8, 11 give quant. ( $\pm 1\%$ ) recovery of Th ( $\approx 30 \text{ mg}$ ), and 9 of these give quant. ( $\pm 2\%$ ) recovery of Zr ( $\approx 20 \text{ mg}$ ) within the pH range 3.5 to 4.8. Mercury, Fe and  $\text{Ce}^{IV}$  interfere; in the presence of Ni, Cr or Co, a double pptn. is necessary. T. R. ANDREW

**5202. 2:5-Dihydroxy-p-benzoquinone as an analytical reagent for the gravimetric determination of thorium and zirconium.** B. D. Jain and S. P. Singhal (Dept. of Chem., Delhi University, India). *Talanta*, 1960, **4** (3), 178-181.—Quadrivalent Th is quant. pptd. as a complex from N  $\text{HCl}$ ;  $\text{Ce}^{4+}$ ,  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  are pptd. at pH 2 to 3 and  $\text{UO}_2^{2+}$  at pH 7 and thus do not interfere. Quadrivalent Zr is also quant. pptd. from N  $\text{HCl}$ ;  $\text{Ti}^{4+}$  do not interfere, but  $\text{Fe}^{2+}$  must be absent. The Th and Zr chelates are ignited to the oxides. Sulphate does not interfere in either determination. R. M. S. HALL

**5203. o-Carboxyphenylazochromotropic acid (sodium salt) as an analytical reagent. I. Chelato-metric titration of thorium, zirconium and iron.** A. K. Majumdar and C. P. Savariar (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1960, **174** (3), 197-200 (in English).—*o*-Carboxyphenylazochromotropic acid (sodium salt) (I) has been successful as an indicator for the direct titration with EDTA (disodium salt) of Th (pH 2.0 to 3.6), Zr (pH 1.4 to 2.8) and  $\text{Fe}^{III}$  (pH 2.0 to 3.8). Alkali and alkaline-earth metals,  $\text{Hg}^{II}$ ,  $\text{Mn}^{II}$ ,  $\text{Cr}^{III}$  and  $\text{UO}_2^{2+}$  do not interfere. As little as 1 mg of Th, 1 mg of Zr or 0.5 mg of  $\text{Fe}^{III}$  may be determined.

**II. Spectrophotometric determination of thorium and aluminium.** A. K. Majumdar and C. P.

Savariar. *Ibid.*, 1960, **174** (4), 269-274 (in English).—The spectrophotometric determination of Th and Al with **I** has been investigated. The metal complexes both absorb strongly at 590 m $\mu$ . The ratios of metal to **I** are 2:3 and 1:1 and the optimum pH ranges are 2.7 to 3.4 and 4.8 to 5.0 for Th and Al, respectively. Beer's law is obeyed for 0.1 to 8 p.p.m. of Th and for 0.1 to 1 p.p.m. of Al. All complexing anions such as  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and oxalate interfere, as do the following cations—Ti, Zr, Ce, Sn, U,  $\text{Fe}^{III}$ , Ni, Co, Bi and Mn; Be affects the determination of Al. An excess of **I** also affects the colour.

T. R. ANDREW  
P. D. PARR-RICHARD

5204. A method for the determination of absolute quantities of ionium (thorium-230). K. B. Zaborenko and N. V. Filippova (M. V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 203-206.—In the proposed method,  $^{230}\text{Th}$  is obtained in a state of radiochemical purity by electrolytic isolation on a platinum cathode, without a carrier, in a form suitable for  $\alpha$ -counting. The electrolyte contains impulse quantities of Th isotopes, 10 to 100 mg of Ce salt, about 1 g of  $(\text{NH}_4)_2\text{SO}_4$  at pH 3.4 and 33% (v/v) of ethanol. The electrolyte temp. is 70°, the cathode c.d. is 200 mA per sq. cm and the electrolysis takes 30 min. The absolute quantity of  $^{230}\text{Th}$  is calculated directly from  $\alpha$ -activity measurements, making necessary corrections, or indirectly by comparison with standard  $^{230}\text{Th}$  preparations.

A. BURWOOD-SMITH

5205. Titration of hydrazine sulphate with permanganate. C. Drotschmann and R. Wyatt (Dept. of Chem., Tech. Univ., Eindhoven, Netherlands). *Chem. Weekbl.*, 1960, **56** (18), 265-266.—Hydrazine sulphate in aq. soln. can be determined by titration with  $\text{KMnO}_4$  in  $\text{H}_2\text{SO}_4$  medium. It can also be oxidised by  $\text{MnO}_2$  in acid and in ammoniacal media, the reaction velocity being determined by the specific properties of the  $\text{MnO}_2$  sample used.

M. J. MAURICE

5206. New reagents for the colorimetric determination of nitrite. L. S. Bark, R. Catterall, O. Meth-Cohn and H. Suschitzky (Royal Tech. Coll., Salford, England). *Chem. & Ind.*, 1960, (14), 375-376.—Heterocyclic nitrogen compounds, viz. N-(2-aminophenyl)piperidine (**I**) and N-(2-aminophenyl)morpholine (**II**) develop, in the presence of  $\text{NO}_2^-$ , deeply coloured, fairly stable soln. of the corresponding diazonium salts. The  $\text{H}_2\text{O}$ -sol. hydrochloride of **I** gives an intense orange-coloured soln. having max. absorption at 445 m $\mu$ . Beer's law is followed from 0.1 to 20  $\mu\text{g}$  of  $\text{NO}_2^-$  per ml. Measurements should be made at 18° to 20° after the reaction mixture has been set aside in the dark for 40 min., and they are valid in the presence of a 100-fold excess of **I** and of various ions, including  $\text{NO}_3^-$ , in concn.  $>200 \mu\text{g}$  per litre. Interference is caused by  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  (in concn.  $>10 \mu\text{g}$  per ml), and  $\text{VO}_2^{2+}$ ,  $\text{MnO}_4^-$  and  $\text{H}_2\text{O}_2$  (in concn.  $>50 \mu\text{g}$  per ml);  $\text{F}^-$  does not interfere and can be used to mask  $\text{Fe}^{3+}$ . The diazo salt formed with **II** has max. extinction at 435 m $\mu$ , the colour intensity becoming constant within  $\approx 30$  sec. The mol. extinction coeff. of the diazonium compounds of **I** and **II** are approx. equal.

W. J. BAKER

5207. Gravimetric determination of phosphate. E. Schulek and A. Endrői-Havas (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Z. anal. Chem.*, 1960, **174** (2), 90-96 (in German).—Studies on the determination of  $\text{PO}_4^{3-}$  by pptn. with

$\text{Mg}^{2+}$  indicate an error of about +0.6% on weighing as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and an error of about -0.3% after ignition of the ppt. and weighing as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Phosphate may be determined in the presence of Ca after addition of the stoichiometric amount of EDTA. Interference due to  $\text{Fe}^{III}$  and  $\text{Al}^{III}$  can be eliminated in the same manner. If  $\text{Fe}^{III}$  alone is present its interference can be prevented by prior reduction to  $\text{Fe}^{II}$  with ascorbic acid.

T. R. ANDREW

5208. Titrimetric method for determining arsenite in presence of arsenate. M. Z. Barakat and A. Abdalla (Fac. of Veterinary Med., Cairo Univ., Giza, Egypt). *Analyst*, 1960, **85**, 288-294.—The method is based upon the quant. oxidation of an aq. soln. of arsenite by N-bromosuccinimide, which is itself irreversibly reduced to succinimide with formation of HBr. To a measured vol. of  $\text{NaAsO}_2$  soln. an equal vol. of 10%  $\text{NaHCO}_3$  soln. and 4% KI soln. are added together with starch indicator soln. The mixture is titrated with 0.1% w/v aq. N-bromosuccinimide until a blue colour indicates the endpoint. If  $v$  is the titre (ml) and  $c$  the concn. of the N-bromosuccinimide soln. (mg or  $\mu\text{g}$  per litre) the  $\text{NaAsO}_2$  present is  $129.92 \text{ } v c / 178$  mg or  $\mu\text{g}$ . Soln. of  $\text{As}_2\text{O}_3$  are titrated similarly, the content being  $197.84 \text{ } v c / 356$  mg or  $\mu\text{g}$ . The advantages claimed over the iodine method are that the reagent is a crystalline compound soluble in hot water without volatilisation, the freshly prepared soln. does not require standardisation, and the experimental error ( $\pm 2\%$ ) is lower.

A. O. JONES

5209. New photometric method for the determination of antimony. G. Ciuhandu and M. Rocsin (Inst. of Hygiene, Timişoara, Romania). *Z. anal. Chem.*, 1960, **174** (2), 118-121 (in German).—Stilbene, generated by reduction of the sample soln. with copper-coated zinc in  $\text{H}_2\text{SO}_4$  soln. (50% by vol.), is passed into an alkaline soln. of Ag  $p$ -sulphamoylbenzoate. A sol. is formed having strong absorption at 420 m $\mu$  (possibly greater at shorter wavelengths). From 1 to 100  $\mu\text{g}$  of Sb may be determined by this method.

T. R. ANDREW

5210. Potentiometric titration of bismuth with sodium and lithium ferrocyanides. H. Basinska and Z. Orylski (Copernicus Univ., Torun, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 187-191.—In both titrations the resulting ppt. has a ratio of  $\text{Bi}^{3+}$  to  $[\text{Fe}(\text{CN})_6]^{4-}$  of 1.472. Optimum results were obtained from well diluted soln. The error for samples of 0.05 to 0.3 g was  $<1.0\%$  as compared with the gravimetric determination as bismuth oxyiodide.

L. SMAKOWSKI

5211. Colorimetric determination of vanadium as vanadyl sulphate. M. Kranz and J. Krzyżniak (Univ., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 243-246.—The method depends on measurement of the blue colour of  $\text{VO}_2^{+}$ ;  $\text{V}^{5+}$  are reduced with  $\text{SO}_2$  in  $\text{H}_2\text{SO}_4$  soln. The colour at first decreases in intensity by  $\approx 3\%$ , and then remains stable. Beer's law is obeyed over the range 0.05 to 0.7 mg of V per ml. Chromium, Co and Ti interfere, but Fe, Mn, Ni, Mo, W, Pb and colourless ions do not. This method is suitable for the rapid determination of V in catalysts used in the manufacture of  $\text{H}_2\text{SO}_4$ .

L. SMAKOWSKI

5212. Determination of vanadium oxides in glass by oxidimetry. I. I. Kitaigorodskii and V. K. Frolov (D. I. Mendeleev Chem.-Tech. Inst., Moscow).

*Zavod. Lab.*, 1960, **26** (4), 418-422.—Vanadium glasses are classified in three groups: (i) glass containing  $V_2O_5$  and  $V_2O_4$ , (ii) glass containing  $V_2O_4$  and  $V_2O_3$ , and (iii) glass containing  $V_2O_5$  and  $VO$ . Methods of determining the groups and the individual oxides are described. G. S. SMITH

**5213. Gravimetric semi-micro determination of vanadium by means of N-(2-hydroxynaphthyl-1-methylene)ethylamine and 2-hydroxynaphthaldoxime.** S. I. Gusev, V. I. Kumov and E. V. Sokolova (Perm. Med. Inst.). *Zhur. Anal. Khim.*, 1960, **15** (2), 180-183.—Vanadium is determined as  $(C_6H_5N:CH-C_6H_4O)_2VO$  and  $(HON:CH-C_6H_4O)_2VO$  with the reagents N-(2-hydroxynaphthyl-1-methylene)ethylamine (I) and 2-hydroxynaphthaldoxime (II). The determination of V in ferrovanadium can be made without preliminary separation of Fe, by using ascorbic acid as reducing agent. Ferrovanadium is dissolved in  $HNO_3$  (sp.gr. 1.2), heated to expel nitrogen oxides, neutralised with 25% aq.  $NH_3$  and diluted to 100 ml with water. To this soln. is added a 2% soln. of I in ethanol, the mixture is heated to boiling and ascorbic acid (1.5 g) is added. The yellow-green ppt. of vanadyl-I is collected on a glass filter, washed 3 times with 50% ethanol and dried at  $110^\circ$ . The conversion factor is 0.10995. The procedure is the same with II, but the conversion factor is 0.11598.

A. BURWOOD-SMITH

**5214. Emission spectrometric determination of the gaseous elements in metals. VI. Oxygen in vanadium.** V. A. Fassel and L. L. Altpeter (Iowa State Univ., Ames, U.S.A.). *Spectrochim. Acta*, 1960, **16** (4), 443-449.—A d.c. carbon arc discharge in argon, and the line pairs O 7772-Ar 7891-A and O 7775-Ar 7891-A, are employed to determine the O content of vanadium metal within the concn. range 0.004 to 0.5% (w/w) with a coeff. of variation of  $\pm 6\%$ . Synthetic standards are prepared by dissolving pure  $V_2O_5$  in vanadium metal of low O content by means of a helium arc melting technique. It is shown that the rate and degree of evolution of the O is dependent on the environmental conditions in the graphite supporting electrode.

G. P. MITCHELL

**5215. Separation and gravimetric determination of niobium, tantalum and titanium by precipitation with N-benzoyl-N-phenylhydroxylamine.** F. J. Langmyhr and T. Hongslo (Univ. Oslo, Blindern, Norway). *Anal. Chim. Acta*, 1960, **22** (4), 301-305.—All three metals are first separated from other elements by double pptn. with N-benzoyl-N-phenylhydroxylamine (I) at pH 1 in the presence of EDTA and tartaric acid, and are recovered as oxides. The oxides are re-dissolved by fusion with  $K_2S_2O_7$  or by treatment with HF, and the Nb and Ta are pptd. with I in the presence of EDTA and  $H_2O_2$ . After re-precipitation by the same procedure, Nb and Ta are separated by a modification of the method of Majumdar and Mukherjee (*cf. Anal. Abstr.*, 1959, **6**, 1699), in which Nb is pptd. at pH 4.5 to 5.0. The filtrates containing Ti are evaporated, the organic content is oxidised with  $HNO_3$ , evaporation is continued to produce fumes of  $H_2SO_4$ , and after dilution to 5%  $H_2SO_4$ , the Ti is pptd. with I and weighed as  $TiO_2$ . H. N. S.

**5216. Spectrographic determination of tantalum in carbides.** V. Hampl and V. Dufek (V.Ú.P.M., Vestec u Prahy, Czechoslovakia). *Hutn. Listy*, 1960, **15** (4), 300-301.—For use with samples con-

taining tungsten carbide as the chief constituent and tantalum carbide (1 to 10%). Co, Ti, and perhaps Cr, the a.c. spark and the condensed spark were compared. Better results were obtained with the condensed spark. The method was carried out with the Zeiss Q24 apparatus, with a copper electrode, and the lines Ta 2685-1 and W 2681-4 A.

J. ZÝKA

**5217. Determination of tantalum in rocks by neutron-activation analysis.** D. F. C. Morris and A. Olya (Brunel Coll. of Technol., London, W.3). *Talanta*, 1960, **4** (3), 194-200.—Tantalum has been determined as  $^{182}Ta$  by  $\gamma$ -scintillation counting. Carrier Ta is added before separation from the dissolved fused material by pptn. as hydrous oxide, dissolution in  $H_2SO_4$ -HF and extraction with tributyl phosphate. The standards are irradiated with the samples as dil. aq. soln. in order to reduce self-shielding effects. Rhenium and W do not interfere at the levels usually found in igneous rocks. The values found for the standard granite (G1) and diabase (W1) rocks (U.S. Geol. Survey) are, respectively, 3.0 and 0.93 p.p.m.

R. M. S. HALL

**5218. Determination of active oxygen in charged metal-ceramic nickel electrodes.** I. S. Mustafin and N. S. Frumina (Chernyševskii Saratov State Univ.). *Zavod. Lab.*, 1960, **26** (4), 410-412.—The sample (wt. not given) is heated for 10 min. with 4 ml of 40% NaOH soln. and 2 ml of a saturated soln. of  $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ , the material is then crushed with a glass rod, a further 4 ml of NaOH soln. is added, and the mixture is heated for 30 min. or until the clean grey colour of metallic nickel appears. The soln. is filtered and the  $CrO_4^{2-}$  formed are titrated iodimetrically or with a soln. of  $Fe^{2+}$  in the presence of N-phenylanthranilic acid, after the addition of  $H_2SO_4$ .

G. S. SMITH

**5219. Determination of sulphide sulphur in minerals.** A. R. Vasudeva Murthy and K. Sharada (Indian Inst. Sci., Bangalore). *Analyst*, 1960, **85**, 299-300.—To the powdered mineral (50 to 100 mg) in the reaction vessel previously described (Murthy *et al.*, *Ibid.*, 1956, **81**, 373) a small drop of mercury is added and the air in the apparatus is displaced by hydrogen. Hydriodic acid (sp. gr. 1.7) ( $\approx 5$  ml) is added and the flask is gently warmed. The  $H_2S$  evolved is swept into an alkaline suspension of  $Cd(OH)_2$  and the determination is continued as previously described (*loc. cit.*). Such minerals as pyrite and chalcopyrite, stibnite and the arsenic sulphide minerals are dissolved rapidly, and the evolution of  $H_2S$  is complete.

A. O. JONES

**5220. Determination of sulphide, hydrosulphide and hydrogen sulphide when present together in pure aqueous solutions.** K. P. Mishchenko, T. A. Tumanova and I. E. Flis (Leningrad Tech. Inst. of Cellulose-Paper Industry). *Zhur. Anal. Khim.*, 1960, **15** (2), 211-217.—The method is based on potentiometric measurement of the pH of soln. containing  $S^{2-}$ ,  $HS^-$  and  $H_2S$ , followed by adding known quantities of pure alkali up to pH 13 and titrating these aq. soln. with  $AgNO_3$ . The concn. of  $S^{2-}$ ,  $HS^-$  and  $H_2S$  are calculated from data obtained from the corresponding thermodynamic equations. It is found that  $AgHS$  and  $Ag_2S$  are formed equally on titrating the sulphide soln.

A. BURWOOD-SMITH

**5221. Infra-red determination of traces of sulphate in reagent chemicals.** I. Citron and A. L. Underwood (Emory Univ., Atlanta, Ga., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (4), 338-344.—Sulphate ions are retained selectively when the test soln. is passed through a column of activated alumina. The  $\text{SO}_4^{2-}$  are eluted with  $M$  aq.  $\text{NH}_3$ .  $\text{KBr}$  (0.3 g) is dissolved in an aliquot of the eluate and the soln. is freeze-dried. The dried residue is compressed into a disc and the i.r. transmittance spectrum of the disc is recorded over the range 7 to 11  $\mu$ . The  $\text{SO}_4^{2-}$  band appears at 9  $\mu$ . The method is applied to the determination of 0.001 to 0.005% of  $\text{SO}_4^{2-}$  in  $\text{KBr}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KMnO}_4$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . Phosphate interferes when its concn. in the original soln. is  $\approx 4$  times that of the  $\text{SO}_4^{2-}$ . H. N. S.

**5222. Analysis of mixtures of sulphuric and nitric acids. Conductimetry.** Y. Lacroix and M. Chaverou. *Mém. Poudres*, 1959, **41**, 423-439 (in French).—A conductimetric apparatus capable of a precision of 0.1% is described. It consists of a container for the sample, thermostatically controlled to  $\pm 0.1^\circ$  and equipped with a cell with bright platinum electrodes, a glass circulating pump and a Wheatstone Bridge circuit operating at 1000 c/s. Equations, graphs and tables are given showing the relationship between conductivity and composition for  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$ - $\text{H}_2\text{O}$  mixtures. When the method is applied to process samples, the results obtained for the water content are  $\approx 5\%$  lower than those given by chemical analysis. This is partly due to the presence of organic impurities. W. T. CARTER

**5223. Separation by distillation and photometric determination of small amounts of selenium.** A. Kotarski and Z. Marczenko (Inst. Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 235-242.—In the procedure described, Se is separated by distillation with  $\text{HCl}$  and  $\text{Br}$  and reduced with  $\text{SnCl}_2$ , and the extinction of the orange colloidal soln. is measured at 390 to 395  $m\mu$ . The effects of gum acacia and gelatin as protective colloids were compared. Selenium (0.1 to 1.0%) was determined successfully in various materials (e.g., waste sulphuric acid, inorganic salts and organic substances). L. SMAKOWSKI

**5224. Phase analysis of lead-production dust for selenium content.** N. A. Filippova, L. A. Martynova, E. V. Savina and R. D. Kulichikhina. *Zavod. Lab.*, 1960, **26** (4), 401-410.—Selective solvents for selenium compounds in mixtures are—methanol for  $\text{SeO}_2$ , 0.5  $M$  acetic acid for  $\text{ZnSeO}_3$ , 0.5  $M$   $\text{NaCl}$  for  $\text{HgSeO}_3$ , 0.5  $M$  citric acid for  $\text{PbSeO}_3$ , 1.5  $M$   $\text{Na}_2\text{SO}_3$  for  $\text{Se}$ , 0.1  $N$   $\text{KBr}$  in 0.1  $N$   $\text{H}_2\text{SO}_4$  for  $\text{ZnSe}$ , 7  $N$   $\text{HNO}_3$  for  $\text{PbSe}$ , and 0.25  $M$  EDTA (disodium salt) for selenites in general. Methods of determining  $\text{Se}$  and its compounds in lead dusts are described. G. S. SMITH

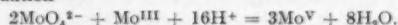
**5225. Determination of aluminium in tellurium by means of an anionite.** N. P. Strel'nikova and V. N. Pavlova. *Zavod. Lab.*, 1960, **26** (4), 425-426.—In a column of  $\text{ÉDE-10p}$  ( $\text{Cl}^-$  form)  $\text{Al}$  is not adsorbed at any concn. of  $\text{HCl}$  in the soln. Over the range 4 to 12  $M$   $\text{HCl}$ ,  $\text{Te}$  is completely adsorbed, but can be eluted by means of more dilute  $\text{HCl}$  soln. G. S. SMITH

**5226. The determination of hexathiocyanato-chromium(III) ions.** P. Spacu, C. Gheorghiu and E. Antonescu (Univ. "C. I. Parhon," Bucharest,

Romania). *Z. anal. Chem.*, 1960, **174** (2), 81-87 (in German).—It is shown that  $\text{Cr}(\text{SCN})_6^{3-}$  may be determined gravimetrically by pptn. of the silver salt from weakly acid ( $\text{HNO}_3$ ) soln., volumetrically by potentiometric titration with standard  $\text{AgNO}_3$  soln., or photometrically by measurement of the extinction of the acid soln. (in water or acetone) at 574  $m\mu$ . Tervalent  $\text{Cr}$  may be determined by conversion into  $\text{Cr}(\text{SCN})_6^{3-}$  by heating the soln. containing  $\text{Cr}^{3+}$  for 1 hr. at  $80^\circ$  in the presence of  $\text{KSCN}$  and a little  $\text{H}_2\text{SO}_4$ . In aq. soln. an extinction of 0.5 is given by 400  $\mu\text{g}$  of  $\text{K}_2\text{Cr}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$  per ml in a 5-cm cell; in acetone soln. the corresponding extinction is 0.3. T. R. ANDREW

**5227. Application of amperometry in kinetic methods of quantitative analysis. I. Catalytic determination of small amounts of molybdenum.** W. Jędrzejewski (Univ., Łódź, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 207-214.—Sexavalent  $\text{Mo}$  catalyses the reaction between  $\text{H}_2\text{O}_2$  (0.001  $M$ ) and  $\text{KI}$  (0.0002  $M$ ) in the presence of  $\text{H}_2\text{SO}_4$  (0.8  $M$ ). The changes in iodine concn. are registered by the current flowing between two polarised platinum electrodes. The curve of current vs. time is linear over a short period (2 to 3 min.) and its slope ( $\alpha$ ) depends on the concn. of  $\text{Mo}$ . A graph of  $\tan \alpha$  vs. concn. of  $\text{Mo}$  is used as a calibration curve. The method was applied to the determination of  $2.8 \times 10^{-8}$  to  $1.4 \times 10^{-7}$  g of  $\text{Mo}$  per ml, and gave reproducible results with an error of  $\pm 6.0\%$ . L. SMAKOWSKI

**5228. Molybdenometry. II. The titration of sexavalent molybdenum by means of tervalent molybdenum solution.** A. I. Busev and Li Gyn (M. V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 191-199.—During titration in a conc.  $\text{HCl}$  medium one mole of  $\text{Mo}^{\text{III}}$  reduces two moles of molybdate according to the equation—



Titration in which a platinum indicator-electrode was used were carried out to study the behaviour of a number of elements in the titration soln. The influence on the titration curves of  $\text{HCl}$  concn. and the presence of  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ , orthophosphoric, silicic, boric, oxalic, tartaric and citric acids in the titration soln. are illustrated. Of the different indicator electrodes investigated, it was found that platinum, platinum amalgam and graphite are satisfactory, but tungsten and tantalum are not recommended. There is no interference from high concn. of  $\text{W}$  provided that the  $\text{W}$  is held in soln. as an oxalate complex in a conc.  $\text{HCl}$  medium. Citric and tartaric acids do not prevent  $\text{W}$  from interfering. There is no interference from  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Cd}$ ,  $\text{Ti}$ ,  $\text{Al}$ ,  $\text{Mg}$ ,  $\text{Bi}$  or  $\text{Te}$  in conc.  $\text{HCl}$  soln., but  $\text{V}^{\text{V}}$  and  $\text{U}^{\text{VI}}$  are reduced and hinder the determination;  $\text{Se}^{\text{IV}}$  is reduced together with  $\text{Mo}^{\text{VI}}$ , and both show the same potential drop;  $\text{Cu}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  behave in the same way as  $\text{Se}^{\text{IV}}$ , and the titre corresponds to the sum of  $\text{Mo}^{\text{VI}}$  with these elements.

A. BURWOOD-SMITH

**5229. Spectrographic determination of molybdenum in tungsten trioxide and tungsten in molybdenum trioxide.** T. M. Moroshkina and Yu. V. Abramichev. *Vestn. Leningr. Univ.*, 1960, No. 10, Ser. Fiz. i Khim., (2), 161-163.—The excitation times at 220 V and 8 amp. with copper electrodes are 40 sec. for  $\text{WO}_3$  and 2 min. for  $\text{MoO}_3$ . Standards are prepared from ammonium tungstate and molybdate in the ranges 0.008 to 0.056% for  $\text{Mo}$  determinations



and 0.03 to 0.104% for W determinations. The line Mo 3132.59 Å is used for Mo in tungsten trioxide. The lines Fe 3132.5 Å and V 3132.59 Å mask the Mo line, but only when the concn. of these elements exceeds 1%. The line W 4008.75 Å is used for W determinations, with Mo 4008.054 Å as internal standard. The method may also be applied to metallic tungsten and molybdenum. The precision is  $\pm 10\%$ .

A. BURWOOD-SMITH

**5230. Determination of uranium by chromatography. I. Paper-chromatographic method.** T. Palágyi (Central Res. Inst. for Chem., Acad. of Sci., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (2), 131-138 (in English).—A semi-quantitative method is described for determining U in the range 0.5 to 200 µg with an error of  $\pm 20\%$ . After a suitable wt. of the sample has been dissolved by a conventional method, the pH is adjusted to 3 and the soln. is diluted to a known vol. Then one or more 0.02-ml drops are transferred to filter-paper strips (Macherey No. 214 is the most suitable), and the chromatograms are developed with ethyl methyl ketone or butyl acetate containing 15% (v/v) of  $\text{HNO}_3$  by an ascending technique. For amounts of  $\text{U} < 5 \mu\text{g}$ , the paper strips should taper upwards from 20 mm to 6 mm wide. When dry, the strips are sprayed with a 5% soln. of  $[\text{Fe}(\text{CN})_6]^{4-}$ , and the intensities of the spots are compared with those of standard spots of U. Other metals do not interfere.

**II. Determination by column chromatography.** T. Palágyi. *Ibid.*, 1960, **22** (3), 239-245 (in English).—In the method of Burstall and Wells (*Analyst*, 1951, **76**, 396), the use of isobutyl methyl ketone (I) containing 2% of  $\text{HNO}_3$  as solvent instead of ethyl ether (II) permits elution of U from cellulose columns without contamination by Fe or V (as oxidized by the peroxides in II). The eluate is freed from I by azeotropic distillation and the U determined photometrically with  $\text{K}_4\text{Fe}(\text{CN})_6$  on a Pulfrich photometer (S47 filter). Thus 0.5 to 5 mg of U is rapidly determined with an error between 3 and 5%. There is no interference from 0.2 mg of V or 1 mg of Fe, Cu, Co or Ni. **Procedure**—Transfer the sample to a 10-cm column of pulp made from Whatman No. 1 paper, and elute with I (80 ml) containing 2% by vol. of  $\text{HNO}_3$ . Dilute the eluate with  $\text{H}_2\text{O}$  (80 ml) and remove I by azeotropic distillation (b.p. 88°). Evaporate the aq. residue, add conc.  $\text{H}_2\text{SO}_4$  (2 to 3 ml) and heat to fuming. Cool, add  $\text{H}_2\text{O}$  (20 ml), 10%  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. (5 ml containing 1% of  $\text{SO}_3^{2-}$ ), make up to 50 ml and compare the extinction with a  $\text{K}_4\text{Fe}(\text{CN})_6$  blank. Read the U content from a calibration curve. J. H. WATON and J. P. STERN

**5231. Potentiometric determination of uranium.** W. Helbig (Zentralinst. für Kernphysik, Bereich Radiochemie, Rossendorf, Germany). *Z. anal. Chem.*, 1960, **174** (3), 169-172 (in German).—Uranium (0.005 to 0.001 M) in  $\text{N H}_2\text{SO}_4$  in the absence of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  is reduced with excess of  $\text{Ti}_2(\text{SO}_4)_3$  soln. and the resulting soln. is titrated with  $\text{Ce}(\text{SO}_4)_2$  soln. The two inflections of the potential vs. volume curve correspond to  $\text{U}^{4+} \rightarrow \text{UO}_2^{2+}$  and  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ , and the content of U is determined from the vol. of  $\text{Ce}(\text{SO}_4)_2$  used between the two end-points. Results for  $\approx 2.5 \text{ mg}$  of U are within  $\pm 0.015 \text{ mg}$  of the added amount, and for 0.1 to 1.5 µg of U recoveries are within 15% of the added amount.

T. R. ANDREW

**5232. Rapid spectrographic determination of uranium in ores by the powder-sifting method.** B. Strzyżewska (Inst. Nuclear Res., Polish Acad.

Sci., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 277-281.—The method, applied to ore leaching residues, consists in introducing the sample into an a.c. arc (6 amp., 220 V) by the powder-sifting method. The line 4090-14 Å was used. Concn. from 0.001 to 0.20% of U were determined with a coeff. of variation of 6-1%.

L. SMAKOWSKI

**5233. Separation of beta- and gamma-radioactive uranium decay products from uranyl nitrate by solvent extraction.** T. S. Urbanski (Inst. Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 283-287.—Uranyl nitrate can be separated from  $\beta$ - and  $\gamma$ -active decay products by extraction with a 40% soln. of tributyl phosphate in kerosene from 4 M  $\text{HNO}_3$  - 3 M HF in the presence of powdered  $\text{Th}(\text{NO}_3)_4$ . Thorium was pptd. as  $\text{ThF}_4$  together with the active isotopes present in uranium;  $\text{UX}_2$  ( $^{234}\text{Pa}$ ) remained in the aq. phase as the fluoride complex together with some radioisotopes. Purification by a factor of  $3 \times 10^3$  was obtained. Extraction in the absence of HF, even from concentrated soln. of U, gave inferior results. Re-extraction of uranium into the aq. phase can be achieved by pptn. as ammonium uranate after the addition of 5-0% aq.  $\text{NH}_3$  and decantation, the ppt. being then filtered off and dissolved in a known amount of  $\text{HNO}_3$ . After purification uranium again rapidly becomes radioactive; in 24 hr. the activity increases from 50 to 850 counts per sec.

L. SMAKOWSKI

**5234. Spectrographic determination of cadmium in uranium oxide by fractional distillation.** L. Pszonicki (Inst. Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 261-268.—The Cd is concentrated and its spectrum separated from that of U, by preliminary fractional distillation from the electrode with  $\text{AgCl}$  as carrier; this can also act as a carrier during the excitation. Cadmium could be detected at a concn. of 0.01 µg per g. Drawings of the electrodes are given.

L. SMAKOWSKI

**5235. Separation of uranium and protactinium from thorium by amine extraction.** Fujio Ichikawa and Shinobu Urano (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Bull. Chem. Soc. Japan*, 1960, **33** (5), 569-575 (in English).—Uranium, Pa and Th are satisfactorily separated from each other by extraction with a secondary amine [a 5% soln. of Amberlite LA-1 (HCl form) in kerosene]. Separation from HCl soln. is superior to that from soln. of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The dependence of the extraction coeff. on the acid concn. is similar to that of the distribution coeff. when an anion-exchange resin (Dowex 1-X8) is used, but extraction is more selective for U. Radiation damage to Amberlite LA-1 is negligible for a total dose of  $> 5 \times 10^7$  roentgen. The method is suggested for the recovery of  $^{233}\text{U}$  from reactor blanket fuel. I. JONES

**5236. Electrolytic separation of trace amounts of uranium, neptunium, plutonium and americium.** A. G. Samartseva. *Atomnaya Energiya*, 1960, **8** (4), 324-329.—Loss of radioactive elements by adsorption on walls of glass or Plexiglas electrolytic cells, which is considerable at certain pH, is largely prevented by using a platinum dish as anode and an oblong platinum foil (1 sq. cm working surface) rotating at 60 to 80 r.p.m. as cathode; deposition takes place simultaneously on both sides of the cathode.  $\alpha$ -Activity of the electrode is recorded by a special counter (Bugorkov et al.,

*Truđý Radiev. Inst.*, 1958, **9**, 214). Tests are carried out with the following molar concn. of isotope in the electrolyte— $1.3 \times 10^{-3}$  of  $^{232}\text{U}$ ,  $0.2$  to  $1.2 \times 10^{-4}$  of  $^{237}\text{Np}$ ,  $4.1 \times 10^{-5}$  of  $^{239}\text{Pu}$  and  $1.4 \times 10^{-10}$  of  $^{241}\text{Am}$ . Macro amounts of the hydroxides are dissolved in  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$  or oxalic acid to serve as electrolytes with a  $\text{H}^+$  concn. of  $10^{-1}$  to  $10^{-4} \text{ M}$ ; the  $\text{H}^+$  concn. of buffered electrolytes is  $10^{-3}$  to  $10^{-2} \text{ M}$ . The yield of the elements by electrolysis is shown to be independent of the anion; the determining factor is the pH of the soln. Ionisation chamber and multi-channel amplitude analysers show that the recovered  $^{239}\text{Pu}$  contains 0.7 to 0.9% of a mixture of  $^{241}\text{Am}$  and  $^{238}\text{Pu}$ , and  $^{237}\text{Np}$  contains  $\approx 2.0\%$  of  $^{239}\text{Pu}$ . No impurity is found in  $^{241}\text{Am}$ ;  $^{232}\text{U}$  is not analysed. Studies of the valency state of the elements in the original soln. show that  $^{232}\text{U}$  is in the hexavalent state;  $^{237}\text{Np}$  consists of 10.2% of  $\text{Np}^{4+}$ ,  $\approx 90\%$  of  $\text{Np}^{3+}$  and  $<1\%$  of  $\text{Np}^{2+}$ ;  $^{239}\text{Pu}$  consists of 14.3% of  $\text{Pu}^{4+}$ , 56.1% of  $\text{Pu}^{3+}$  and 28.9% of  $\text{Pu}^{2+}$ ;  $^{241}\text{Am}$  is in the trivalent condition. Curves and tables of the experimental data are given. *Electrolytic recovery of Pu in the presence of other ions*—Evaporate an aliquot (0.1 to 5 ml) of the original soln. to dryness on a water bath. Treat the residue with conc.  $\text{HNO}_3$  ( $\times 2$  or 3). Add  $\text{M}$  oxalic acid (0.1 ml) to eliminate interference from Fe and 0.5  $\text{M}$   $\text{HNO}_3$  (10 ml) and set aside on a water bath for 10 to 15 min., keeping the platinum dish covered with a watch-glass. Add  $\text{H}_2\text{O}$  (30 ml) to the dish and electrolyse for 1.5 to 2 hr. with a cathode c.d. of 1 amp. per sq. cm. The recovery was  $99.9 \pm 0.7\%$ . K. R. C.

**5237. Application of X-ray fluorescence methods to the in-line determination of uranium and plutonium concentrations.** K. J. H. Mackay and R. P. Thorne (U.K.A.E.A., Research and Development Branch, Capenhurst). U.K.A.E.A. Report DEG 134 (CA), 1960, 30 pp.—From a review of the literature it is concluded that there are important advantages in the use of a radioactive source, preferably of  $^{241}\text{Am}$ , to excite the fluorescence spectra. The analysis of the radiation could be achieved by the use of a proportional counter containing xenon and an electronic pulse amplitude analyser, and if necessary the radiations from U and Pu could be measured separately by fitting filters of platinum, iridium and gold to the counters.

G. J. HUNTER

**5238. Quantitative analysis of the surface oxidation of uranium and uranium carbide powders by means of X-rays.** M. Pluchery (Centre D'Études Nucléaires, Grenoble, France). *Planseeber. Pulvermet.*, 1960, **8** (1), 14–21 (in French).—The ratio of the intensity of the Bragg reflection of an X-ray beam from spherical uranium and uranium carbide granules to the theoretically calculated total reflection is shown to be a function of thickness of the surface oxide layer. An X-ray absorption procedure, based on this, has been used satisfactorily to determine layer thicknesses  $>0.02 \mu$  on samples of known oxide content. Results with powders have shown a similar oxide-layer thickness for granules of different diameters, whilst reputedly pure uranium powders showed the presence of a thin  $\text{UO}_2$  film.

G. P. MITCHELL

**5239. Study of actinides. I. Determination of the content of americium-241 in plutonium by spectroscopy of  $\alpha$ - and  $\gamma$ -radiation.** J. Malý, H. Kurzweilová, R. Lenk and I. Peka (Inst. of Nucl.

Res., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1382–1390 (in German).—The methods and results for the determination of traces of  $^{241}\text{Am}$  in the presence of  $^{239}\text{Pu}$  by spectroscopy of the  $\alpha$ - and  $\gamma$ -radiation, in plutonium, materials containing 0.032% of  $^{241}\text{Am}$  and in enriched mixtures containing 0.69 or 3.6% of  $^{241}\text{Am}$  are described. By means of  $\alpha$ -spectroscopy a minimum amount of 0.02% of  $^{241}\text{Am}$  was determined, whereas  $\gamma$ -spectroscopy permits the determination of 0.001%. J. ŽYKA

**5240. Spectrophotometric determination of fluoride using lanthanum chloranilate.** Kiyoko Hayashi, Taeko Danzuka and Keihei Ueno (Dojindo and Co. Ltd., Kumamoto, Japan). *Talanta*, 1960, **4** (2), 126–132 (in English).—Metathesis of the lanthanum salt of chloranilic acid (I) with  $\text{F}^-$  yields insol.  $\text{LaF}_3$  and liberates free I, which is determined spectrophotometrically at 530  $m\mu$ ; 2 to 200 p.p.m. of  $\text{F}^-$  can be determined to within  $\pm 2\%$ . The method is applicable to organic F compounds after they have been decomposed by the flask combustion method of Schöniger (*Anal. Abstr.*, 1955, **2**, 1816; 1956, **3**, 3660). *Procedure*—To the sample (0.2 to 10 mg of  $\text{F}^-$ ) add 0.3  $\text{M}$  Na succinate (pH 7) (10 ml), 95% ethanol (50 ml) and the solid lanthanum salt of I (0.2 g), and dilute to 100 ml. Shake for 20 min., filter, and determine the extinction of the middle portion of the filtrate. Read the  $\text{F}^-$  content from a calibration curve. J. P. STERN

**5241. Voltammetric, potentiometric and amperometric studies with a rotated aluminium wire electrode. V. Amperometric titration of fluoride with aluminium.** I. M. Kolthoff, E. J. Meehan and C. J. Sambucetti (Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (4), 351–363.—The rotated aluminium electrode (cf. Kolthoff *et al.*, *Anal. Chim. Acta*, 1960, **22**, 253) is used in the amperometric titration of  $\text{F}^-$  in concn. between  $10^{-4}$  and  $2 \times 10^{-3} \text{ M}$ . The titrant is a standard soln. of  $\text{Al}(\text{NO}_3)_3$  and the medium is buffered at pH 3.6 to 4.6. Equilibrium for each reading is established in 5 to 15 min. and the end-point is determined graphically. The  $\text{F}^-$  to  $\text{Al}$  ratio at the end-point increases from 2.2 for  $10^{-4} \text{ M}$   $\text{F}^-$  to 2.8 for  $2 \times 10^{-3} \text{ M}$   $\text{F}^-$ . When the titration is carried out in an acetate buffer of pH 4.0 in 50% ethanol in the presence of 0.5  $\text{M}$   $\text{KNO}_3$  or  $\text{NaNO}_3$ , the end-point is independent of the concn. of  $\text{F}^-$  and corresponds to a  $\text{F}^-$  to  $\text{Al}$  ratio of 5.8  $\pm$  0.1. H. N. S.

**5242. Contaminant absorption bands in the infra-red spectra of inorganic fluorides.** W. R. Heslop, J. A. A. Ketelaar and A. Büchler (A. D. Little, Inc., Cambridge, Mass., U.S.A.). *Spectrochim. Acta*, 1960, **16** (4), 513.—When working with inorganic fluorides and other halides, absorption bands due to  $\text{Na}_2\text{SiF}_6$  at 13.75  $\mu$  and of  $\text{SiF}_4$  at 9.7  $\mu$  and 8.3  $\mu$  are frequently observed. Evidence is given that  $\text{SiF}_4$  may be present as an impurity in commercial samples, or may be formed during manipulation by the action of the fluoride on glassware, whilst  $\text{Na}_2\text{SiF}_6$  arises from the action of  $\text{SiF}_4$  on sodium chloride cell windows. G. P. MITCHELL

**5243. Detection of periodate in the presence of iodate.** A. Berka (Dept. Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (4), 1224–1225.—Mix 1 ml of luminol soln. (0.1 g in 10 ml of conc. aq.  $\text{NH}_3$ , filtered and diluted to 100 ml with  $\text{H}_2\text{O}$ ), 0.5 ml of  $\text{H}_2\text{O}_2$  soln. (3%) and 4 ml of  $\text{H}_2\text{O}$ . The addition of periodate produces



a violet fluorescence. As little as 2  $\mu\text{g}$  of  $\text{KIO}_4$  in 1.5 ml can be detected. Iodates do not react in a similar way and even in large excess do not interfere.

J. ŽYKA

**5244. Extraction methods for the rapid separation and quantitative determination of small amounts of ferric and ferrous iron.** K. H. Lieser and H. Schroeder (Eduard-Zintl-Inst. für Anorg. und Phys. Chem., Tech. Hochschule, Darmstadt, Germany). *Z. anal. Chem.*, 1960, **174** (3), 174-179 (in German).—Ferric iron may be extracted from soln. at pH 5 to 6 by acetylacetone in  $\text{CCl}_4$ , and the extinction of the extract measured at 420  $\mu\text{m}$ ; ferrous iron is complexed with 2:2'-dipyridyl and the extinction of the aq. phase measured. Results on mixtures containing up to 500  $\mu\text{g}$  of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  show recoveries within 5% of added amounts, and it is possible to determine relatively small amounts of  $\text{Fe}^{\text{II}}$  in the presence of relatively large amounts of  $\text{Fe}^{\text{III}}$ , e.g., in the ratio of 1 to 100. Care must be taken to remove air from all soln.

T. R. ANDREW

**5245. Analytical applications of complexones.** VIII. Absorptiometric and spectrophotometric micro-determination of iron with 1:2-diaminocyclohexane-NNN'-tetra-acetic acid. F. Bermejo Martínez and R. Rey Mendoza. *An. Real Soc. Esp. Fis. Quim.*, B, 1959, **55**, 293-298.—In the micro-determination of Fe with 1:2-diaminocyclohexane-NNN'-tetra-acetic acid (disodium salt) (I) the absorption of the chelate follows Beer's law. Graphs are given of the absorption spectrum of the I- $\text{Fe}^{3+}$  chelate at different pH, the calibration curve, the variation of extinction with pH, and the chelate stability against time. An interpretation of the results is given. The main interferences are pointed out.

**X. Iodimetric determination of iron(II) in the presence of 1:2-diaminocyclohexane-NNN'-tetra-acetic acid.** F. Bermejo Martínez and R. Rey Mendoza. *Ibid.*, 1959, **55**, 305-308.—A new method for the determination of Fe in the presence of I is proposed. This method gives results in good agreement with those of the classical ones. A new normal potential  $E^\circ$  for the  $\text{FeY}^{2-} + e \rightleftharpoons \text{FeY}^{3-}$  system is established. The variation of the oxidation potential with pH and the stability of the I- $\text{Fe}^{3+}$  chelate have been studied.

CHEM. ABSTR.

**5246. Coulometric permanganometric determination of ferrocyanide and iodide ions.** P. S. Tutundžić, N. M. Paunović and M. M. Paunović (Belgrade Univ., Yugoslavia). *Anal. Chim. Acta*, 1960, **22** (4), 345-350 (in German).—Ferrocyanide ions (4 to 33 mg) are titrated with  $\text{MnO}_4^-$  electrolytically generated from  $\text{MnSO}_4$  in 6 to 8 N  $\text{H}_2\text{SO}_4$ . Iodide ions (3 to 10 mg) are titrated similarly in 4.5 N  $\text{H}_2\text{SO}_4$ . Both titrations are conducted at constant current with potentiometric end-point detection.

H. N. S.

**5247. Methods for the analysis of iron and steel.** Part 41: Lead in carbon steel and low alloy steel. British Standards Institution (2 Park St., London, W.1). B.S. 1121:Part 41:1960. 6 pp.—Lead is separated as sulphide and determined gravimetrically as lead molybdate. The new method supersedes Part 1c of B.S. 1121.

**5248. Application of gas-phase chromatography to the determination of hydrogen, nitrogen and oxygen in steel and cast iron.** P. Tyout (Centre Nat.

de Rech. Métallurgiques, Madrid). *Inst. Hierro y Acero*, 1960, **13**, 383-391.—After a brief review of the principles of gas-phase chromatography, the application of this technique to the analysis of synthetic mixtures of H, N and CO and of the gases obtained by vacuum fusion of metals is described. Argon is used as the carrier gas; when H is used as carrier for the determination of CO and N, the peak heights are increased 9- and 10-fold, respectively. Detection is by a differential thermal conductivity detector block.

G. H. FOXLEY

**5249. Review of methods for determination of lead in cast iron.** R. C. Rooney (B.C.I.R.A., Res. Dept., Alvechurch, Birmingham). *B.C.I.R.A. Journal*, 1960, **8** (3), 360-376.—A review and critical investigation of published methods for determination of Pb in concn. of 0.0001 to 0.01% is reported. Tl. colorimetric dithione and extraction-polarographic methods give interference-free results. The square-wave polarographic method of Ferrett and Milner (*Analyst*, 1956, **81**, 193) gives accurate results if the interference from Sn is eliminated and corrections are made for Tl. Gravimetric methods are not considered likely to give accurate results. Direct polarographic methods are satisfactory for Pb contents high enough to render the effects of Sn, Tl, As and Mo negligible, but at Pb contents of the same order as those of the elements named it is considered unlikely that correction factors could be applied. (24 references.)

C. H. COWPER-COLES

**5250. Analysis of cementite in chrome steels by measuring the magnetic properties.** W. Koch, W. Jellinghaus and H. Rudhe (Max-Planck Inst. for Iron Res., Düsseldorf). *Arch. Eisenhüttenw.*, 1960, **31** (3), 183-188.—In a method for determining the Cr content of cementite in chromium steel, the chromium carbides are separated electrolytically from the steel, and the magnetic properties of the separated carbides are measured. *Procedure*—A 30-mg sample of the separated carbides is filled into a small tube ( $\approx 3$  mm diam. and  $\approx 30$  mm long), and the tube is sealed after removing air by vacuum and heating to expel absorbed gases. By means of the magnetic balance of Mathieu (*Ibid.*, 1942-43, **18**, 415) the curve of magnetisation vs. temp. of the sample is obtained over the range  $0^\circ$  to  $300^\circ$ , and the Cr content is fixed from the Curie point (i.e., the point of intersection of the tangent of the curve at the turning point with the temp. axis). A graph of Curie point vs. Cr content is given. The method is accurate to 2 to 3% and is not affected by the crystalline state of the carbide.

H. L. WHITEHEAD

**5251. Rapid semi-micro gravimetric method for the determination of cobalt in complex compounds by decomposition with hydrogen peroxide in alkaline medium.** E. Bogdan, M. Moțaș and D. Giurgiu (Inst. Chem. "Petru Poni," Iași, Romania). *Stud. Cercet. Științ. Chim.*, Iași, 1959, **10** (2), 195-198.—*Procedure*—Conc.  $\text{H}_2\text{O}_2$  is prepared by heating a 30% soln. on a water bath at  $65^\circ$  until it begins to give off bubbles of gas (30 to 40 min.). The sample is treated with 1 to 2 ml of NaOH soln. (80% w/v), followed by cautious dropwise addition of 1 ml of the hot conc.  $\text{H}_2\text{O}_2$ . When reaction is complete, the fine brown cryst. ppt. of  $\text{Co}_3\text{O}_4$  is allowed to settle, collected in a G4 filter, washed 4 to 5 times with hot water, and dried at  $105^\circ$ . The method was checked by converting the  $\text{Co}_3\text{O}_4$  into  $\text{CoCl}_2$  and determining the Co with sodium 1-nitroso-2-naphtholsulphonate. Results showed errors  $\pm 0.3\%$ .

H. SHER

5252. **Determination of cobalt as selenite.** V. D. Anand and G. S. Deshmukh (Benares Hindu Univ., Varanasi, India). *J. Sci. Ind. Res., India, B*, 1960, **19** (3), 103-105.—A known excess of 0.5 M sodium selenite is added to the sample soln. (1 to 120 mg of Co) at pH 8 to 9; the mixture is heated for  $\approx 1$  hr. at 60° and is then put aside for 3 to 4 hr. to convert the amorphous cobalt selenite into the cryst. form. The ppt. is collected in a sintered glass filter, washed with water, dried at 105° to 110° and weighed as  $\text{CoSeO}_4 \cdot 2\text{H}_2\text{O}$ . The result can be confirmed by iodimetric determination of the excess of  $\text{Na}_2\text{SeO}_3$ . The method is simple and rapid; the error ranges from +1.5% to -9%. W. J. BAKER

5253. **Alkaline ferri cyanide titration of cobalt in dilute solutions.** V. D. Anand (Chem. Lab., Benares Hindu Univ., Varanasi, India). *Z. anal. Chem.*, 1960, **174** (3), 192-193 (in English).—The potentiometric determination of cobalt in alkaline soln. by titration with  $\text{Fe}(\text{CN})_6^{4-}$  is satisfactory for concn. of Co down to 0.00001 M. T. R. ANDREW

5254. **Determination of trace quantities of cobalt by polarography, spectrophotometry and neutron activation.** D. Monnier, J. Vogel, H. Haerdi and P. E. Wenger (Lab. de Chim. Minérale et Anal., Univ. de Genève, Switzerland). *Chimia*, 1960, **14** (4), 128 (in French).—A critical comparative review of the three techniques is presented. E. G. CUMMINS

5255. **Determination of small amounts of iron, manganese and copper in nickel.** W. Kemula, K. Brajter, S. Cieplik and A. Lipińska-Kostrowicka (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 229-234.—In the method described, Cu was determined polarographically. Iron and Mn were pptd. as hydroxides on Lewatite MII anion-exchange resin, previously washed with aq.  $\text{NH}_3$ . Nickel and other cations (e.g., Co, Cu and Zn) appeared in the percolate as ammonia complexes. Iron and Mn were eluted with  $\text{H}_2\text{SO}_4$  and determined colorimetrically, Fe with thiocyanate and Mn as permanganate. Determinations of Cu (0.5 to 1.0%), Fe (0.03 to 1.0%) and Mn (0.03 to 1.0%) had an accuracy of  $\approx \pm 3\%$ . L. SMAKOWSKI

5256. **Determination of palladium with 2-hydroxy-1-naphthaldehyde.** A. S. Pesis and Z. A. Bitovt (Perm Med. Inst.). *Zhur. Anal. Khim.*, 1960, **15** (2), 200-202.—Palladium is pptd. with 2-hydroxy-1-naphthaldehyde in a  $\text{HNO}_3$  medium (pH 2.5 to 3), without heating, and determined gravimetrically in the form of a yellow ppt. of  $\text{C}_{10}\text{H}_7\text{O}_2\text{Pd}$ . It is possible to determine Pd in the presence of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  at ratios up to 1:100,  $\text{Cd}^{2+}$  up to 1:50,  $\text{Fe}^{3+}$  up to 1:15,  $\text{Ag}^{+}$  up to 1:20 and  $\text{Pt}^{4+}$  up to 1:2. The cations  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Be}^{2+}$  react with 2-hydroxynaphthaldehydes only in an alkaline medium. A. BURWOOD-SMITH

5257. **Spectrophotometric determination of osmium. III. 2-Aminophenol-p-sulphonic acid as a reagent.** A. K. Majumdar and J. G. Sen Gupta (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (4), 306-310.—2-Aminophenol-p-sulphonic acid yields a brown colour with  $\text{Os}^{\text{VI}}$  and  $\text{Os}^{\text{VIII}}$ . The absorption max. is at 440 m $\mu$  and the mol. extinction coeff. are 15,690 for  $\text{Os}^{\text{VI}}$  and 19,500 for  $\text{Os}^{\text{VIII}}$ . The colour develops in 30 min.

at a temp. of 34° and at an optimum pH range of 2.5 to 4.0. Beer's law is followed for 1 to 10 p.p.m. of Os;  $\text{Ru}^{4+}$ ,  $\text{Rh}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ca}^{2+}$  interfere at a 1:1 ratio, and the permissible amounts of nine other cations are limited. The optimum range, accuracy and sensitivity of the method and the mol. ratio and dissociation constant of the complex are determined. H. N. S.

5258. **Separation of noble metals and tellurium from sulphate solutions [obtained from electrolytic slimes].** T. N. Greiver. USSR Pat. 126,875 (10.3.60).—Enriched slimes from the electrolysis of copper are ignited at 600° to 650° (when containing Pt) or at 550° (when containing Au and Ag), and the residue is treated with  $\text{H}_2\text{SO}_4$ , which dissolves 85 to 90% of the Te, most of the Cu, and some of the noble metals. The soln. is treated with Cu, Ni or other suitable metal powder at room temp. to precipitate noble metals (Au, Ag, Pt) and most of the Se; after filtering, the soln. is heated to boiling and again treated with the metal powder to precipitate Te. C. D. KOPKIN

5259. **Quantitative mineralogical analysis by X-ray powder diffraction.** W. A. Mitchell (Macaulay Inst., Craigiebuckler, Aberdeen, Scotland). *Miner. Mag.*, 1960, **32**, 492-499.—In the procedure described,  $\text{Co K}\alpha$  radiation is used, and absorption difficulties are overcome by using thin diluted specimens containing an internal standard. An arbitrary universal intensity scale has been established with KCl as the primary internal standard; values for the stronger lines of a number of minerals are given. N. E.

See also Abstracts—5126, Microbiological methods for trace metals. 5128, Microoxy fatty acids as reagents for Th, Zr and Fe. 5129, Oxine N-oxide as reagent for U. 5131, 5132, Metalochromic indicators. 5310, Detection of Mg. 5336, Potassium salts in explosives. 5471, CO in air. 5483, Sulphur in iron and steel. 5519, Automatic analysis of U fission products.

### 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.*

5260. **Use of various metal oxides in organic elementary analysis.** W. J. Kirsten (Inst. f. Med. Chem., Univ. Uppsala, Sweden). *Z. anal. Chem.*, 1960, **174** (4), 282-285 (in German).—The use of  $\text{CuO}$ ,  $\text{NiO}$  and  $\text{Co}_3\text{O}_4$  as tube packings is discussed with particular reference to the work of Kainz and Hainberger (*Anal. Abstr.*, 1960, **7**, 2748). The following method of preparing  $\text{Co}_3\text{O}_4$  for the determination of N is given. Reduce the metal powder or carbonate in H for 20 min. at 800° and cool under H. Transfer rapidly to a thimble and extract with boiling  $\text{H}_2\text{O}$  overnight. Dissolve in the minimum amount of conc.  $\text{HNO}_3$  and evaporate, then decompose about 50 g of the nitrate by heating over a flame. Finally heat at 800°. Nickel oxide prepared in this way contains N even after

heating to 950°. It is better prepared from a slurry of NiO and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , dried at 150° and ignited in O at 1000°.

P. D. PARR-RICHARD

**5261. Decomposition of organic substances with magnesium. VIII. Elementary carbon as a source of error in halogen determination in organic substances.** J. Jeník, M. Jureček and V. Pátek (Dept. Anal. Chem., Inst. Chem. Technol., Pardubice, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1450–1457 (in German).—The influence of elementary C on the micro-determination of halogens after decomposition of the sample with magnesium, and the influence of Fe on the determination of iodine were studied. The interference of C can be avoided by the addition of  $\text{Al}^{3+}$  (Jeník *et al.*, *Anal. Abstr.*, 1960, **7**, 3794) (or of  $\text{Fe}^{3+}$  for the determination of Cl or Br) which desorb the halides from the C. A small amount of Fe in the magnesium used does not influence the results.

J. ZÝKA

**5262. Radiometric analysis of volatile organic compounds labelled with carbon-14 and hydrogen-3 by vapour-phase chromatography.** F. Cacace and Inam-Ul-Haq (Centro di Stud. per la Chimica Nucleare, Roma, Italy). *Ric. Sci.*, 1960, **30** (4), 501–508.—The technique (described in detail) is satisfactory for the separation and determination of volatile labelled compounds boiling below about 150°. The initial separation is effected on a conventional vapour-phase chromatography column with a thermal-conductivity detector. The effluent vapours are then further diluted with carrier gas to a constant flow of 10 litres per hr. and passed to an ionisation chamber of the Borkowsky type, operating at ambient temperature, and connected to an electrometer. The electrometer response is recorded on a chart operated at the same speed as that for the thermal-conductivity recorder. The sensitivity is sufficient to detect a few  $\mu\text{mC}$  of  $^3\text{H}$  or 0.5  $\mu\text{mC}$  of  $^{14}\text{C}$  and for quantitative results with amounts  $>20 \mu\text{mC}$  or 2  $\mu\text{mC}$ , respectively.

E. C. APLING

**5263. Determination of nitrogen in organic compounds by the indanetrione hydrate [ninhydrin] method.** S. Jacobs (National Inst. for Med. Res., Mill Hill, London). *Analyst*, 1960, **85**, 257–264.—Serum and protein hydrolysates are digested with  $\text{H}_2\text{SO}_4$  in micro Kjeldahl flasks; solid samples are sealed with the acid in glass ampoules encased in brass tubes, which are placed in a wrought-iron cylinder and heated at 460° to 480°. The catalyst used is a mixture of  $\text{K}_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{HgO}$  and Se (15:5:5:1). The cooled digest is neutralised with a pre-determined amount of conc. NaOH soln. and adjusted to a known vol. (5 ml) with a citrate buffer soln. of pH 5.0. Aliquots (0.25 ml) are diluted to 2 ml with the buffer soln., and are heated in a water bath for 30 min. with 2 ml of an indanetrione hydrate reagent (prep. described). The cooled liquid is diluted to 10 ml with aq. ethanol (1:1, v/v) and the extinction is measured at 570  $\mu\text{m}$ . The relation between the extinction and the concn. of  $\text{NH}_3$  in the sample is linear. Ultra-micro amounts can be determined by reduction of the vol. of sample, together with corresponding reductions of the reagents; 0.56  $\mu\text{g}$  of N in a 0.2-ml aliquot can then be determined with satisfactory accuracy.

A. O. JONES

**5264. Analysis of fluoro-organic compounds. The simultaneous micro-determination of fluorine, carbon and hydrogen by means of pyrohydrolysis.** N. E. Gel'man, M. O. Korshun and K. I. Novozhilova (Inst. of Elem. Org. Comp., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 222–226.—It has been established that the F retained when fluoro-organic compounds are burned with  $\text{MgO}$  can be quant. removed by means of pyrohydrolysis and determined by titration. When the compounds are burned without  $\text{MgO}$ , the F is retained on the quartz vessel in amounts proportional to the surface area of the vessel and can be removed by pyrohydrolysis. The simultaneous micro-determination of C, H and F in various organic compounds is possible. Nitrogen, P, Si, B, S, Cl and Br do not interfere.

A. BURWOOD-SMITH

**5265. Simultaneous colorimetric micro-determination of chlorine and bromine in organic substances.** A. Sauciuc (Acad. R.P.R., Iași, Romania). *Stud. Cercet. Stiinf. Chim., Iași*, 1959, **10** (2), 199–206.—A method is proposed for the determination of traces of the chlor- and brom-tetracyclines present in tetracycline obtained by fermentation. *Procedure for standard curve*—Aliquots of standard soln. of Cl or Br are diluted to 15 to 18 ml with water and treated with 2.5 ml of a 0.6% methanolic soln. of  $\text{Hg}(\text{SCN})_2$  and 2.5 ml of a 12% soln. of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  in  $\text{HNO}_3$  (12 N). The same amount of reagents is added each time to eliminate the effect of their Cl content. The mixture is cooled to  $20^\circ \pm 1^\circ$  and diluted to 25 ml with water. The extinction is read 10 min. after addition of reagents in a 5-cm cell with a S47 filter, with the reagents as blanks. *Procedure for determination*—From 1 to 25 mg is treated in the oxidation flask with 0.5 to 0.8 g of the oxidising mixture (4 parts of  $\text{K}_2\text{Cr}_2\text{O}_7$  and 1 part of  $\text{AgNO}_3$ ); in the absorption vessel is placed 10 ml of 2%  $\text{H}_2\text{O}_2$  and in the funnel of the oxidising vessel 3 ml of conc.  $\text{H}_2\text{SO}_4$ . The apparatus is assembled, the bulb of the oxidation vessel is heated to 120° to 130°, and the conc.  $\text{H}_2\text{SO}_4$  is admitted to the reaction flask. After 15 min. a weak current of air washed in 25% KOH is passed through the apparatus for 15 min. The absorbent is then washed out, a 10-ml aliquot is taken and treated with 0.3 ml of N NaOH and  $\approx 0.1 \text{ g}$  of  $\text{MnO}_2$ . When the decomposition of the  $\text{H}_2\text{O}_2$  is complete (10 to 15 min), 1 ml of N  $\text{H}_2\text{SO}_4$  and  $\approx 0.1 \text{ g}$  of  $\text{PbO}_2$  are added, and the whole is heated on the boiling-water bath for 10 min. with stirring, cooled and filtered and diluted to 25 ml. The measurement of extinction ( $E_1$ ) corresponding to the Cl content is then determined as for the preparation of the standard curve. A further 10 ml of the absorbent liquid is treated directly as for the standard curve to determine the extinction corresponding to the combined Cl + Br contents ( $E_2$ ). The Cl content is calculated from the value of  $E_1$ , corresponding to the standard curve of Cl, the Br content from the corresponding value of  $E_2 - E_1$  on the Br standard curve.

H. SHER

**5266. Gas-liquid chromatographic separation of chloro derivatives of propane and propene.** M. Singliar, A. Bobák and J. Brida (Res. Inst. for Petrochemistry, Nováky, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (3), 209–214.—Allyl chloride in the presence of other chloro derivatives was determined with the use of a gas-chromatographic column (2 metres  $\times$  6 mm) filled with kieselguhr saturated with 16.7% of triphenyl phosphite. Thermal conductivity was used for the detection and nitrogen as carrier gas.

The lower separation efficiency of tritoyl phosphate compared with triphenyl phosphate is discussed.

J. ZÝKA

**5267. Identification of hydrocarbons by gas chromatography.** R. A. Hively. *J. Chem. Engng Data*, 1960, **5**, 237-240.—Retention times for 93 compounds on dimethylsulpholane, tritoyl phosphate, di-*n*-decyl phthalate, mineral oil and 2:2'-oxydipropionitrile are tabulated. From these data it is possible to identify most of the hydrocarbons, if their identity is unknown, by analysis on these columns.

FUEL ABSTR.

**5268. Separation of isomeric alcohols by means of gas-liquid chromatography.** Separation of saturated  $C_8$  alcohols. F. Kuffner and D. Kallina (Univ. Vienna). *Monatsh. Chem.*, 1959, **90**, 463-466.

—Under suitable conditions, mixtures containing all 8 possible  $C_8$  alcohols were separable into 7 groups. Simpler mixtures gave even better results. The pair 2-methylbutan-1-ol (I) and 3-methylbutan-1-ol (II) were not separable. The retention times in the mixture did not correspond exactly with those of the pure compounds. The vapour-phase chromatographic apparatus contained columns 8 mm in diam. and 182 cm in length. The retention times were measured from the height of the curves. The stationary phase was Carbowax 300 on Celite 545 (3:10) made into a paste, dried and screened (125 to 500  $\mu$ ). With a flow rate of carrier gas (N) of 3 litres per hr. and a column temp. of 100°, a mixture of all 8 isomeric amyl alcohols was separable, except for I and II and in many cases 3-methylbutan-2-ol (III) and/or pentan-3-ol (IV) from pentan-2-ol (V). 2-Methylbutan-2-ol (VI) was detectable in a 1:100 mixture with V. The retention times of the pure compounds did not correspond to those of the alcohols in the mixture. Results are given for the retention times (in min.) of the pure isomers and of all isomers in a mixture—VI, 5, 5-2; 2,2-dimethylpropanol (VII), 8, 8-2; III, 8-8, 9-2; IV, 9-6, 9-2; V, 10-8, 10-8; I, 15-2, 15-2; II, 16-0, 15-2; pentan-1-ol 19-2, 19-4. With a stationary phase of castor oil-Celite (1:5) treated as above, a flow rate of 3 litres per hr. and a column temp. of 102° the following results were obtained—VI, 3-6, 3-4; VII, 4-4, 4-4; III, 5, 5-4; IV, 7-6, 8-6; V, 6-4, 8-6; I, 9-2, 11; II, 9-4, 11; pentan-1-ol, 13-1, 13-2. With a stationary phase of wool fat-Celite (1:5) treated as above, a flow rate of 3-4 litres per hr. and a column temp. of 100°, a mixture of the 8 isomeric amyl alcohols showed six steep peaks, I and II and also VI and III being inseparable. A mixture of III, IV and V gave three distinctly separate peaks.

CHEM. ABSTR.

**5269. Refractometric determination of *tert*-butyl alcohol in complex mixtures with water, secondary and primary alcohols.** B. V. Ioffe and A. I. Borisov (A. A. Zhdanov Leningrad State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (2), 227-230.—The determination of *tert*-butyl alcohol in the presence of primary and secondary alcohols can be carried out by selectively converting it into the chloride and measuring the refractive index of the mixture of the chloride with a weighed quantity of benzene. The accuracy is within  $\pm 0.2$  to 0.4%.

A. BURWOOD-SMITH

**5270. Identification of organic compounds. XXXIV. Identification of aliphatic ethers.** M. Jureček, M. Hubík and M. Večeřa (Dept. Anal. Chem., Inst. Chem. Technol., Pardubice, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960,

**25** (5), 1458-1467 (in German).—The reactions (i) with HI and (ii) with 3:5-dinitrobenzoic anhydride in the presence of  $SnCl_4$  as catalyst were found to be the most suitable for the identification of aliphatic ethers on the micro scale. In (i) alkyl iodides are formed from both alkyl groups, which can then be converted into the alkyl esters of 3:5-dinitrobenzoic acid by reaction with its silver salt. In (ii) the esters are formed directly. The esters were separated by paper chromatography. The methods were tested on 15 ethers and gave unsatisfactory results with asymmetric ethers having isomeric alkyl groups. The mechanism of the reactions is discussed.

J. ZÝKA

**5271. Two methods for determination of hydroxyethoxypropanediol.** J. L. Truchement, A. Ferry-Wilczek and J. P. Parenteau. *Mém. Poudres*, 1959, **41**, 49-55.—3-(2-Hydroxyethoxy)propane-1:2-diol (I) can be determined by esterification with acetic anhydride followed by hydrolysis with a known excess of standard alkali. Water is removed by azeotropic distillation with xylene in a Dean and Stark apparatus, and the esterification is carried out on the residue after the removal of the excess of xylene. The method requires 4 hr. and has a reproducibility of 1%, but gives results  $\approx 2\%$  low. I can also be oxidised with  $NaIO_4$  but, since no acidity is produced, the procedure is based on a determination of the excess of  $NaIO_4$  with KI and 0.1 N  $Na_2AsO_3$ . This method also has a reproducibility of 1%, and a determination can be completed in 1.5 hr.

W. T. CARTER

**5272. Contribution to the analysis of monoglycerides and free glycerol.** L. Hartman (Fats Res. Lab., D.S.I.R., Wellington, New Zealand). *Fette, Seif., Anstrichmitt.*, 1960, **62** (4), 271-274.—The methods of Becker and Krull (*Ibid.*, 1958, **60**, 449) and Pohle and Mehlenbacher (*J. Amer. Oil Chem. Soc.*, 1950, **27**, 54) together with a partition method (*Ibid.*, 1957, **34**, 301) are discussed. A modification of the partition method is described which is based on the titration of  $IO_3^-$  in the presence of  $IO_3^-$  with  $Na_2S_2O_3$  in neutral soln. *Procedure*—The sample ( $\approx 0.6$  g) of  $\alpha$ -monoglyceride is dissolved in 100 ml of  $CHCl_3$  and shaken vigorously for 1 to 2 min. with 100 ml of  $H_2O$  or 5% acetic acid soln. After separation, 25 ml of reagent (5.5 g of  $HIO_4$  dissolved in 50 ml of  $H_2O$  and made up to 1 litre with glacial acetic acid) is added to 25 ml of the  $CHCl_3$  soln. and set aside in the dark for 30 min. Buffer soln. (150 g of NaOH and 100 g of  $Na_2B_4O_7$  per litre of  $H_2O$ ) (100 ml), and, after cooling, 20 ml of 15% KI soln. are added, and the liberated iodine is titrated with 0.1 N  $Na_2S_2O_3$ . As the  $HIO_4$  is only reduced to  $HIO_3$ , the titration of the blank is  $\approx 11$  ml and that of the sample 2 to 5 ml. The glycerol is determined in the same manner in 25 ml of the aq. layer. Results are given and compared with those obtained by titration in acid soln. (original partition method). Conc. from 5 to 9% of  $\beta$ -ester were found in commercially available monoglycerides. The difficulties in determining diglycerides by means of the hydroxyl value in the presence of known quantities of monoglycerides and free glycerol are confirmed.

I. DICKINSON

**5273. Identification of organic compounds. XXXIII. Paper-chromatographic identification and separation of polyhydric alcohols, their esters and chlorohydrins.** J. Borecký and J. Gasparík (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960,



25 (5), 1287-1292 (in German).—The method was developed for alcohols in the free state and after their conversion into esters of 3:5-dinitrobenzoic acid. *Chromatography of free glycols*.—Separate the sample (0.3 to 1.5 mg dissolved in 30% ethanol) on Whatman No. 3 paper with ethyl acetate satd. with  $H_2O$  or with ethyl acetate-ethanol- $H_2O$  (12:2:1) and detect the separated compounds with 5%  $AgNO_3$  soln. - conc. aq.  $NH_3$  (9:3); after drying the paper at  $100^\circ$ , black spots appear on a brown background. The chromatograms can be fixed by washing with  $H_2O$  and moistening with a 10% thiourea soln. in 0.1 N  $H_2SO_4$ . For the detection of vicinal polyhydric alcohols, spraying first with satd.  $KIO_4$  soln. and then with N NaOH - 2% triphenyltetrazolium chloride soln. (1:1) is recommended. After drying the paper at  $100^\circ$ , red spots appear on a pale-pink background. *Chromatography of esters of 3:5-dinitrobenzoic acid*.—Dissolve the derivatives, prepared in the usual way, in benzene and chromatograph on paper impregnated with an ethanolic soln. of formamide (20%) or dimethylformamide (25 or 50%). Hexane or cyclohexane is used as the mobile phase for papers impregnated with dimethylformamide; for papers impregnated with formamide various solvents can be used, e.g., hexane, cyclohexane, benzene,  $CHCl_3$ , ethyl acetate and their mixtures. The spots are detected with a soln. of *p*-dimethylaminobenzaldehyde after reduction of the nitro group with  $SnCl_4$  (Borecký et al., *Anal. Abstr.*, 1959, 6, 1778). J. ZÝKA

5274. Determination of sugars by means of paper chromatography. N. Hellström. *Kungl. Lantbruks-Högskol. Ann.*, 1959, 25, 47-55.—The sugars were separated on chromatograms and treated with different reagents (aniline, diphenylamine, aniline hydrogen phthalate or anthrone) giving coloured spots with sufficiently different absorption spectra to enable quant. measurements to be made for sugars which would otherwise be difficult to separate in closely adjacent spots, e.g., glucose, mannose and fructose. A technique of uniform heating of chromatogram strips (after immersion in reagent) on a smooth heated surface at a controlled temp. for a controlled time is also described.

SUGAR IND. ABSTR.

5275. Analysis of 1:2-glycols and polyhydric compounds. IV. Direct iodimetric determination of fructose through the aldehyde formed on periodic acid oxidation. L. Maros and E. Schulek (Inst. f. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, *Acta Chim. Acad. Sci. Hung.*, 1960, 22 (3), 359-365 (in German).—Oxidation of fructose (I) with  $HIO_4$  in aq. ethanol containing  $H_3PO_4$  affords 2 mol. of aldehyde which is determined by the iodimetric sulphite-cyanide method (cf. *Anal. Abstr.*, 1959, 6, 4823). The accuracy on 50 mg of I is within  $\pm 0.5\%$ . *Procedure*.—To the soln. (10 ml) of I (0.04 to 0.05 g) add 96% ethanol (10 ml) and 20%  $H_3PO_4$  (2 ml). Then add 5 to 6 ml of 0.3 M  $HIO_4$  containing 90 g of  $Na_2H_2IO_6$  per litre of 5%  $H_2SO_4$ , and shake for 30 min. Add 1.5 M  $Na_2SO_3$  dropwise from a pipette until the brownish colour is discharged and then an excess of 0.5 to 0.7 ml, and make weakly alkaline to methyl red with 20% NaOH soln. Acidify with 10% acetic acid (1 ml beyond neutrality), cool with shaking, add pentane (5 to 10 ml), and dilute with  $H_2O$  to 70 ml. After 30 min. titrate the excess of  $H_2SO_4$  first with 5% aq. iodine soln. and near the end-point with 0.1 N iodine (starch indicator). Let the pentane separate, add 20% NaOH soln. (3 ml) and solid KCN (0.3 g).

After 3 min. acidify with HCl and titrate with 0.1 N iodine. Each ml of 0.1 N iodine is equiv. to 4.504 mg of I. J. P. STERN

5276. Estimation of 3-deoxy sugars by means of the malonaldehyde-thiobarbituric acid reaction. M. A. Cynkin and G. Ashwell (Lab. of Biochem. and Metab., Nat. Inst. of Arthritis and Metab. Dis., Bethesda, Md., U.S.A.). *Nature*, 1960, 186, 155-156.—The method of Waravdekar and Saslaw (*Anal. Abstr.*, 1960, 7, 1848), modified by carrying out the periodic acid treatment at  $55^\circ$  for 20 to 25 min., can be used as a general method of assay of 3-deoxy sugars. The calibration curve is linear for quantities of 0.001 to 0.04  $\mu$ mol.

H. F. W. KIRKPATRICK

5277. Contrast staining and quantitative determination of mucopolysaccharides on filter-paper by means of colloidal iron. A. Káhn (Univ. Med. School, Szeged, Hungary). *Stain Technol.*, 1959, 34, 249-256.—The contrast between the Prussian blue colour of the mucopolysaccharide (I) spots and the paper background was increased by differentiation of the paper strips (dyed in acid colloidal iron soln. made up in 60% ethanol) with thioglycolic acid. By this means the  $Fe^{3+}$  bound to the paper background were reduced, but those adsorbed by the I were pptd. as ferric ammonium thioglycollate. This procedure was found to work equally well with acid (including sulphated) and neutral I, even though these varieties exhibited different staining properties by the periodic acid-Schiff and toluidine blue dyeing procedures. Staining of different depolymerisation products of hyaluronate was little influenced by their chain lengths. Determination of the I content of the spots was performed by elution of ferrocyanide with hot NaOH soln. and measurement of the Prussian blue colour of the extracts, developed on acidification and addition of  $FeCl_3$ . CHEM. ABSTR.

5278. Liquid-liquid partition chromatography. Separation of the 2:4-dinitrophenylhydrazones of saturated aldehydes, methyl ketones, 2-enals and 2:4-dienals. E. A. Corbin, D. P. Schwartz and M. Keeney (U.S. Dept. Agric., Washington, D.C.). *J. Chromatography*, 1960, 3 (4), 322-329 (in English).—Two systems are described. Methyl cyanide or 2-chloroethanol is used as the stationary phase on a Celite column with hexane satd. with methyl cyanide or 2-chloroethanol as the mobile phase. The fractions are analysed spectrophotometrically and the majority of the recoveries range from 92 to 102%. Graphs showing the separations obtained for each of the four homologous series are given.

G. P. COOK

5279. Polarographic determination of pyruvaldehyde. J. Krupička and J. K. Novák (Dept. Org. Synth., Chem. Inst. Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, 25 (5), 1275-1279 (in German).—The polarographic behaviour of pyruvaldehyde in acid and buffered soln. was studied. The observed polarographic wave corresponds to the reduction of the aldehyde group; it is of kinetic character and its height decreases with time. For analytical purposes a medium 0.08 M in  $Na_2HPO_4$  and 0.01 M in  $Na_2PO_4$  (pH 10.85) is recommended, in which the change is very slow. In all the pyruvaldehyde soln. analysed, the presence of pyruvic acid (1 to 3%) was detected by a wave at negative potential; this can be distinguished from pyruvaldehyde in supporting electrolytes of pH 3-6 to 5.6. J. ZÝKA

5280. **Rapid paper chromatography of carboxylic acids.** G. Hammarberg and B. Wickberg (Org. Chem. Inst., Kungl. Tek. Högsk., Stockholm, Sweden). *Acta Chem. Scand.*, 1960, **14** (4), 882-884 (in English).—Straight-chain fatty acids up to  $C_{14}$  and other (including sesquiterpenoid) acids are readily separated within 2 hr. by descending paper chromatography on paper impregnated with dimethyl sulphoxide. Solvents used are ethyl ether, light petroleum and isopropyl ether.

J. P. STERN

5281. **Chromatographic separation of N-2:4-dinitrophenylhydrazides of lower fatty acids.** Tokuchiro Seki (Med. Sch., Osaka Univ., Japan). *J. Chromatography*, 1960, **3** (4), 376-377 (in English).—The N-2:4-dinitrophenylhydrazides of nine lower fatty acids were successfully separated on Amberlite IRC-50 ( $H^+$  form) with ethyl methyl ketone-acetone-water (2:1:9). The u.v. absorption of each fraction was measured at 340 m $\mu$ ; recoveries ranged from 97 to 105%.

G. P. COOK

5282. **Polarographic determination of glyoxylic acid.** V. D. Bezugl'yi, V. N. Dmitrieva, T. S. Tarasyok, V. P. Polyakov and N. A. Izmailov (A. M. Gorky State Univ. Kharkov). *Zhur. Anal. Khim.*, 1960, **15** (2), 231-233.—A method is suggested for the analysis of soln. obtained when glyoxylic acid is prepared industrially by the reduction of oxalic acid in the presence of S. The soln. (10 ml) containing glyoxylic acid, oxalic acid and S is neutralised to phenolphthalein with a tetra-alkylammonium base and diluted with  $H_2O$  to 100 ml. To an aliquot of the soln.  $N MgCl_2$  is added, and after passing a stream of  $H$  through the soln. it is polarographed for oxalic acid. Glyoxylic acid is determined by adding buffer soln. of pH 12 to an aliquot of the neutral soln., passing  $H$  and polarographing at 17°.

A. BURWOOD-SMITH

5283. **Mass-spectrometric studies. V. Methyl esters of monoalkyl-substituted acids with ethyl or longer side-chain and methyl esters of di- and polyalkyl-substituted acids.** R. Ryhage and E. Stenhagen (Karolinska Inst., Stockholm 60). *Ark. Kemi*, 1960, **15** (4), 333-362.—Full details are given in graphs and tables of the mass spectra of 25 compounds.

VI. **Methyl esters of normal-chain oxo-, hydroxy-, methoxy- and epoxy-acids.** R. Ryhage and E. Stenhagen. *Ibid.*, 1960, **15** (6), 545-574.

5284. **Determination of the actual content of acid chloride in the chlorides of carboxylic acids.** K. Burger and E. Schulek (L. Eötvös Univ., Budapest, Hungary). *Talanta*, 1960, **4** (2), 120-125 (in English).—The sample is treated with an excess of anhyd. ethanol and the amount of alkali required to saponify the resulting ester is taken as a measure of the acid chloride content of the sample. The  $HCl$  formed and the free acid content of the sample can be determined volumetrically on the esterification mixture and are a check for the presence of unexpected impurities. The relative error for 0.05 to 0.2 g of acyl chloride is within  $\pm 1\%$ . The method is applied to palmitoyl, acetyl, chloroacetyl and benzoyl chlorides. *Procedure*—Weigh the sample into a flask containing anhyd. ethanol (20 ml), heat for 5 min. on a water bath and then cool in ice. Titrate the free  $HCl$  and the organic acid content (to methyl red and phenolphthalein, respectively) with 0.1  $N NaOH$  (for acid chlorides of strong acids a modified titration method is employed). Add

0.1  $N NaOH$  (1.5 to 2 times the vol. used in the titrations) and ethanol if necessary to clear the soln. Heat on a water bath for 1 hr. and back-titrate the excess of  $NaOH$ .

J. P. STERN

5285. **Estimation of small amounts of amines by means of cationite paper.** A. Lewandowski and A. Jarczewski (Dept. of Gen. Chem., Poznań Univ., Poland). *Talanta*, 1960, **4** (3), 174-177 (in English).—Cationite paper [filter-paper with 2 to 10% of phenolsulphonic ion-exchange resin ( $H^+$  form) incorporated therein] (cf. Witkowski, *Anal. Abstr.*, 1957, **4**, 1386) is used in a modified paper-chromatographic procedure. The zones on the paper strip (10 mm  $\times$  80 mm) are detected with suitable reagents, and the amount of amino compound is determined from the area of the coloured zone. The graphs of area (sq. mm) vs. wt. ( $\mu g$ ) of compound are linear. The error is 3%. Results are quoted for 17 compounds.

R. M. S. HALL

5286. **Identification of organic compounds. XXXII. Identification and separation of aliphatic primary amines as N-alkyl-3:5-dinitrobenzamides.** M. Večeřa, B. Voláková, M. Kozáková and M. Jureček (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1281-1285 (in German).—The method was tested on 11 aliphatic amines. After conversion of the amines into N-alkyl-3:5-dinitrobenzamides, the products were isolated and separated by paper chromatography, and their  $R_F$  values and m.p. were determined. *Procedure*—To the soln. of the sample (100 mg) in  $CHCl_3$  (5 ml) add, with cooling, 3:5-dinitrobenzoyl chloride (200 mg), shake for 20 min. with 40%  $K_2CO_3$  soln. (1 ml) and set aside for 12 hr. Separate the  $CHCl_3$  layer, extract the aq. layer twice with  $CHCl_3$  (1 ml), unite the  $CHCl_3$  extracts and dry them with  $Na_2SO_4$ . Evaporate to  $\approx 1$  ml and add light petroleum (4 ml); collect and dry the ppt. The isolated products were dissolved in benzene (if necessary with addition of dioxan) and separated chromatographically on Whatman No. 1 paper impregnated with formamide, with benzene-cyclohexane (2:1) as the mobile phase. The detection was carried out by spraying with 1-naphthylamine soln. (1% in ethanol); the spots were observed in u.v. light (red fluorescence).

J. ŽYKA

5287. **Colorimetric micro-determination of dimethylnitrosamine and dimethylhydrazine.** Y. Le Duigou. *Mém. Poudres*, 1959, **41**, 317-330 (in French).—Determination of dimethylnitrosamine—Dimethylnitrosamine (I) in soln. can be determined colorimetrically by the Griess-Ilosvay reaction. To the sample soln. in dimethylformamide (2 ml containing 4 to 100  $\mu g$  of I) add sulphuric acid soln. (0.3 g in 25 ml of conc.  $HCl$  and 75 ml of dimethylformamide) (1.5 ml) and 0.1% 1-naphthylamine soln. in dimethylformamide (1.5 ml). Heat on a boiling-water bath for 10 min., cool under running water for 1 min. and measure the extinction at 520 m $\mu$ . Under these conditions the precision is 3 to 4% but the sensitivity can be doubled and the precision improved to 1 to 2% by using  $CHCl_3$  to prepare the sample soln. If a spectrophotometer is used to measure the extinction a sensitivity of 1 p.p.m. can be obtained. The method can be used for the determination of I in the atmosphere, with dimethylformamide as the scrubbing soln., and aq. soln. can be analysed by extraction into  $CHCl_3$ . Recoveries of 88 to 95% are quoted for the extraction of 2 ml of aq. soln. with 6 ml of  $CHCl_3$ . High



results are obtained with urine samples owing to the co-extraction of interfering substances, and the lower limit of detection is 10 p.p.m. **Determination of dimethylhydrazine**—Dimethylhydrazine (II) reacts with  $\text{KIO}_3$  in acid soln. with the liberation of iodine, which is determined colorimetrically as the starch complex. To the sample soln. (2 ml, containing 30 to 40  $\mu\text{g}$  of II) add 1%  $\text{KIO}_3$  soln. (2 ml) and 5% soluble starch soln. (1 ml). Mix, add 0.05 N  $\text{H}_2\text{SO}_4$  (1 ml) and measure the extinction at 580  $m\mu$  exactly 15 min. later. If < 30  $\mu\text{g}$  of II is present no colour is obtained. Traces of II in the atmosphere can be determined by aspiration through 0.05 N  $\text{H}_2\text{SO}_4$ , followed by a slightly modified colorimetric procedure. W. T. CARTER

5288. **Determination of dimethylnitrosamine and dimethylhydrazine applied to process control.** C. Monard and C. Garrigues. *Mém. Poudres*, 1959, **41**, 359-368 (in French).—**Determination of dimethylhydrazine**—Acid soln. of dimethylhydrazine (I) containing KBr can be brominated by the addition of 0.1 N  $\text{KBrO}_3$  in the cold; 2 atoms of Br per mol. of I are absorbed rapidly but if an excess of  $\text{KBrO}_3$  is added 8 atoms are absorbed. Titrimetric procedures can be based on both reactions. To the sample soln. (10 ml) containing  $\approx 0.015$  g of I and stabilised with  $\text{H}_2\text{SO}_4$  (0.015 ml) add 5 N  $\text{H}_2\text{SO}_4$  (20 ml) and solid KBr (2 g). Titrate slowly with 0.1 N  $\text{KBrO}_3$  until the yellow colour of free Br appears. Add an excess of 0.1 N  $\text{KBrO}_3$  equal to 3 times the initial titre plus 3 ml and set aside for 15 min. Add 0.5 M KI (10 ml) and water (50 ml), shake, set aside for 2 min. and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The effects of dilution, acid concn. and excess of  $\text{KBrO}_3$  are illustrated. Ammonia and dimethylamine do not interfere, but dimethylnitrosamine interferes seriously and must be absent. The method based on the absorption of 8 atoms of Br gives results  $\approx 2.5\%$  low, whilst a second method (described) based on the absorption of 2 atoms of Br gives results  $\approx 2\%$  high. **Determination of dimethylnitrosamine**—Dimethylnitrosamine (II) gives a clearly defined polarographic wave ( $E_1 = -0.87$  V vs. the S.C.E.). The basal electrolyte is 0.16 M in  $\text{H}_2\text{SO}_4$  and 0.16 M in  $(\text{NH}_4)_2\text{SO}_4$  and may contain up to 390 p.p.m. of II. Dimethylhydrazine and tetramethyltetrazene do not interfere in concn. up to 926 p.p.m. and 773 p.p.m., respectively, but are added to the calibrating soln. (616.3 and 773.2 mg per litre, respectively) to compensate for minor errors. W. T. CARTER

5289. **Photometric determination of barbituric and 2-thiobarbituric acids.** N. S. Drozdov and V. P. Krýlov (N. I. Pigorov Second Moscow State Med. Inst.). *Zhur. Anal. Khim.*, 1960, **15** (2), 248-249.—The reaction of barbituric and 2-thiobarbituric acids with  $\text{NaNO}_2$  in 0.01 to 0.001 M soln. give rise to coloured Na violurates and 2-thioviolurates with max. extinctions at 520 and 570  $m\mu$ , respectively. The reaction is carried out at pH 5.2 for barbituric acid and pH 4.9 for 2-thiobarbituric acid, buffering with phosphate - nitrate or acetate. The reaction mixtures are heated at  $100^\circ$  for 15 min. and immediately cooled to  $20^\circ$ . In this way the colour obtained is sufficiently stable at  $20^\circ$  for several hours. Cations of heavy metals (Cu, Fe) interfere. A. BURWOOD-SMITH

5290. **Use of thiosemicarbazides in analysis. III. Titrimetric determination of thiosemicarbazides with mercuric nitrate.** N. V. Koshkin (Technol. Inst. of Food Industry, Leningrad). *Zhur. Anal. Khim.*,

1960, **15** (2), 147-150.—A quant. determination of thiosemicarbazide (I), and aryl- (II) and diarylthiosemicarbazides (III) is provided by titration with  $\text{Hg}(\text{NO}_3)_2$ , with a cupric salt or diphenylcarbazon as indicator. **Procedure for determination of I**—Prepare an approx. 0.02 M aq. soln. of I, add an equal vol. of acetic acid and 10 to 15 drops of 0.05 M cupric nitrate and titrate with 0.05 M  $\text{Hg}(\text{NO}_3)_2$  to the disappearance of the blue colour. When diphenylcarbazon is used as indicator, titrate without the addition of acetic acid. **Procedure for the determination of II**—Proceed as for I but dissolve samples of 1-phenylthiosemicarbazide in 70 to 80%, and III in 90 to 98%, acetic acid. Add 1 to 2 drops of cupric nitrate soln. for each 10 to 20 ml of test soln. and titrate with  $\text{Hg}(\text{NO}_3)_2$  soln. The colour change at the end-point for 1-phenylthiosemicarbazide, 1:4-diphenylthiosemicarbazide and 1-phenyl-4-*o*-tolylthiosemicarbazide is blue to yellow and for 4-*p*-methoxyphenyl-1-phenylthiosemicarbazide is blue to orange.

A. BURWOOD-SMITH

5291. **Method for identification of alkyl(aryl)-mercury groups and for quantitative determination of mercury in N-organomercury compounds.** B. Hetnarski and K. Hetnarska (Inst. for Org. Synth., Polish Acad. Sci., Warsaw). *Roczn. Chem.*, 1960, **34** (2), 457-463.—The method is based on the reaction of N-organomercury compounds with thiols, whereby S-aryl(alkyl)mercury compounds are quant. produced. **Identification**—The sample ( $\approx 0.001$  mole) is dissolved in abs. ethanol (8 to 20 ml) and treated with a thiol [2-mercaptobenzothiazole (I), 2-mercaptobenzoxazole or 2-mercaptobenzimidazole]. After boiling for 5 min., the soln. is treated with the stoichiometric amount of Na ethoxide in 3 ml of ethanol and diluted with  $\text{H}_2\text{O}$  till a permanent turbidity is formed. The soln. is then cooled and the cryst. ppt. is filtered off, washed with  $\text{H}_2\text{O}$  and identified by its m.p. **Determination**—The sample ( $\approx 0.1$  g) is treated with 0.01 N ethanolic I (sodium salt) (25 ml), heated to boiling and then mixed with half-satd. NaCl soln. (200 ml). The ppt. is filtered off and washed with NaCl soln. (200 ml). The united filtrate and washings are treated with 1% Na acetate soln. (10 ml) and the excess of I is titrated with 0.01 N iodine, with starch as indicator. The error is  $\pm 0.3\%$  and the determination takes 2 hr.

W. MIAKOWSKI

5292. **Infra-red spectra of some methyl derivatives of germanium and tin.** M. P. Brown, R. Okawara and E. G. Rochow (Harvard Univ., Cambridge, Mass., U.S.A.). *Spectrochim. Acta*, 1960, **16** (5), 595-601.—The i.r. spectra between 400 and  $1500\text{ cm}^{-1}$  of dimethylgermanium oxide (trimer, tetramer and high polymer), dimethylgermanium sulphide (trimer), bis(trimethylgermanium) oxide, dimethyltin oxide, dimethyltin sulphide (trimer), methyltin oxide and 1:3-dichlorotetramethyldistannoxane are reported, and all but that of the trimer of dimethylgermanium oxide are shown.

E. G. CUMMINS

5293. **Determination of benzene by the method of Hofmann and Höchtlén.** J. C. Maire (Inst. de Chim., Strasbourg, France). *Bull. Soc. Chim. France*, 1959, (11-12), 1924.—The method of Hofmann and Höchtlén (*Ber.*, 1903, **36**, 1149) for the determination of benzene by pptn. as  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5$  is investigated by thermogravimetry and determination of  $\text{NH}_3$  (by Kjeldahl) and Ni (as anthranilate). The pH of the pptn. is critical and should be  $10.5 \pm 0.05$ . At lower pH,  $\text{Ni}(\text{CN})_2$  is co-pptd., and, at

higher pH, pptn. is not quant. Thermogravimetry shows no step for the complex itself, but steps at 100° to 160° for  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3$ , at 250° for  $\text{Ni}(\text{CN})_2$ , and at 290° for Ni. The pptd. complex is therefore dried for 2 to 3 hr. at 110° and weighed as  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3$ ; the precision is  $\approx 1\%$  for benzene if the mixture is free from thiophen and furan.

E. J. H. BIRCH

**5294. Determination of styrene as pseudonitrosite.** V. Sedivec and J. Flek (Inst. Hyg. and Ind. Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1293-1300 (in German).—Styrene (I) is converted with  $\text{NaNO}_2$  in glacial acetic acid into styrene pseudonitrosite [(2-nitro-1-nitrosoethyl)benzene], which is polarographically active and yields a well-developed wave ( $E_1 = -0.27$  V). The method is suitable for the determination of 0.01 to 10 mg of I with an accuracy of  $\pm 3\%$ . The presence of aromatic and aliphatic carbohydrates, halogen derivatives of carbohydrates, aldehydes, alcohols, ketones, esters and some unsaturated compounds causes no interference. *Procedure*—Dissolve the sample (0.25 to 25 mg of I) in 25 ml of glacial acetic acid. To 10 ml of this soln. add  $\text{NaNO}_2$  soln. (50%) (0.5 ml), mix and set aside for 15 to 20 min. at room temp. Dilute with  $\text{H}_2\text{O}$ , add Na acetate soln. (50%) (5 ml) and gelatin soln. (0.5%) and make up to 25 ml with  $\text{H}_2\text{O}$ . Remove O with a stream of N and register the polarographic wave from 0 to  $-0.45$  V. Compare with a calibration curve.

J. ZÝKA

**5295. Determination of cymene and *tert*-butyltoluene isomers by infra-red absorption spectra.** Yu. Ya. Mikhallenko, N. N. Lebedev and I. K. Kolchin (D. I. Mendeleev Chem.-Technol. Inst., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 159-162.—A method of absorption i.r. spectrophotometry used by Kaye and Otis (*Anal. Chem.*, 1948, **20**, 1006) is applied to the analysis of *o*-, *m*- and *p*-cymenes and *tert*-butyltoluenes. The coeff. of variation of the determination of individual components in a three-component mixture of *o*-, *m*- and *p*-cymenes is 1.5 to 2%, and in a mixture of *o*-, *m*- and *p*-*tert*-butyltoluenes is 2 to 3%.

A. BURWOOD-SMITH

**5296. Absorptiometric determination of phenol.** F. W. Ochynski (D.S.I.R., Nat. Chem. Lab., Teddington, Middx., England). *Analyst*, 1960, **85**, 278-281.—The sample soln. (5 ml), filtered or centrifuged if necessary, is treated with 10 ml of satd.  $\text{Na}_2\text{B}_4\text{O}_7$  soln. and 1 ml of 4-aminophenazone soln. (3% w/v), followed by a further 10 ml of  $\text{Na}_2\text{B}_4\text{O}_7$  soln. and 1 ml of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  soln. (2% w/v). After 10 min. the mixture is made up to 50 ml and the extinction is measured against a blank soln. containing no phenol, in a Spekker absorptiometer with Ilford No. 604 filters, and referred to a calibration graph. The max. extinction in the presence of  $\text{Na}_2\text{B}_4\text{O}_7$  is at 540  $\mu$ . Calcium, magnesium and iron salts, amino acids and peptides do not interfere. From 2 to 20 p.p.m. of phenol in aq. soln. can be determined with an accuracy within  $\pm 5\%$ .

A. O. JONES

**5297. Analysis of phenols by gas-phase chromatography.** A. Kreyenbuhl and H. Weiss (Cherchar, Verneuil-en-Halatte, France). *Bull. Soc. Chim. France*, 1959, (11-12), 1880-1885.—The retention vol. of a number of phenols ( $\text{C}_6$  to  $\text{C}_9$ ) are measured by gas chromatography on a Pyrex-glass column (11 metres  $\times$  7 mm), with C22 brick (Johns Manville

0.35 to 0.55 mm) as support and usually St-Gobain vacuum grease SI (petrol-insol. fraction removed) as stationary phase. The usual temp. is 165° and the carrier gas H. Detection is effected by a recording katharometer and 5 to 100 mg of sample is used. The introduction of alkyl groups into the nucleus of a phenol can affect the retention vol. by its effect on the mol. wt. (the hydrogen bonding causing association), the acid dissociation const. of the phenol, and the resonance energy. The chromatograms can be used quant. by the method of measuring the peak surface area, provided that H and not N is used as carrier gas. An example is given of the analysis of 9 distillation fractions of phenols from the hydrogenation of coal.

E. J. H. BIRCH

**5298. Paper chromatography of phenols with polyamide-impregnated paper.** K.-T. Wang (Dept. of Chem., National Univ., Taiwan). *Riechststoffe u. Aromen*, 1960, **10** (5), 158-159 (in German).—In a paper-chromatographic method for separating and identifying mono- or poly-hydric phenols in mixtures containing one or more of them, the paper used is previously impregnated with polycaprolactam. *Procedure*—To prepare the paper, filter-paper is saturated with a 5% soln. of the polymer in 80% formic acid; the impregnated paper is pressed between filter-paper to remove excess of acid, then dried in air overnight, and finally heated under i.r. for 15 to 20 min. to remove residual acid. A soln. of the phenol-containing sample is developed by the descending technique, and the phenol or phenols are identified by treating the spots with diazotised sulphanilic acid, or from their  $R_F$  values. The preferred solvents are hydrocarbons for monohydric phenols, ethyl acetate for di- or tri-hydric phenols, and butanol for trihydric phenols. The  $R_F$  values for 14 different phenols in 7 different solvents are given. The use of the method for separating and identifying *o*- and *p*-cresol, carvacrol and phenol with cyclohexane as the solvent is described.

H. L. WHITEHEAD

**5299. Electrophoresis. VI. Paper electrophoresis of phenols.** H. Berbak and I. Szabolcs (Tech. Hochsch., Vienna). *Monatsh. Chem.*, 1959, **90**, 198-205.—The sodium salts of phenols and thiophenols were subjected to electrophoresis on paper-chromatographic strips in a soln. of 0.05 N NaOH with barbitone buffer at 20 to 25 V per cm. For easily oxidised phenols, 2%  $\text{Na}_2\text{SO}_3$  soln. was added to the soln., which changed the pH and relative migration. The strips were dried and treated with diazotised sulphanilic acid in 0.05 N HCl, tetrazotised dianisidine (alkaline), or  $\text{FeCl}_3$  in dil. HCl, depending on which gave the best visible identification. Nitrophenols gave their own colour, and Pb acetate was used for thiophenols. Separation of a mixture required 20 to 30 min. Relative migrations were based on that of 1-naphthol. Study of the effect of change of pH on relative migration showed that at pH 6.9 most phenols have a value close to 0, and the value increases with increase in pH. Sulphonic acid coupling dyes were separated by electrophoresis at a lower optimum pH than phenols. Relative migration could not be related to structure and could be related only partially to dissociation constants.

CHEM. ABSTR.

**5300. Infra-red absorption spectra of phenol and dihydric phenols.** A. Hidalgo and C. Otero (Inst. de Óptica "Daza de Valdés," Madrid, Spain).

*Spectrochim. Acta*, 1960, **16** (5), 528-539 (in French).—The spectra obtained between 5000 and 250  $\text{cm}^{-1}$  for these solids in discs, in mulls and in frozen mulls are compared, and assignment of the absorption bands is attempted. E. G. CUMMINS

**5301. Comparative detoxication. VIII. The metabolism of chlorobenzene in locusts: phenolic metabolites, a comparison with some vertebrate species.** [Determination of *o*-, *m*- and *p*-chlorophenol.] T. Gessner and J. N. Smith (St. Mary's Hosp. Med. Sch., London, England). *Biochem. J.*, 1960, **75** (1), 172-179.—Mixtures of *o*-, *m*- and *p*-chlorophenol are separated on a column of Hyflo Supercel- $\text{Na}_2\text{CO}_3$ . The mixture is applied in *n*-hexane, and development and elution are effected with *n*-hexane-isopropyl ether (15:1). The recovery of *o*-chlorophenol is 80 to 95%, and that of *m*- plus *p*-chlorophenol 98 to 102%. When the ratio of *p*- to *m*-chlorophenol is <5, the recovery of either isomer is within  $\pm 10\%$ . *o*-Chlorophenol is determined by measurement of its u.v. absorption in 0.1 *N* NaOH at 294  $\mu$ . A mixture of *m*- and *p*-chlorophenol is determined in 0.1 *N* NaOH at 299  $\mu$  where both isomers have the same extinction coeff., and the total amount is ascertained from a standard graph prepared by use of either isomer. For the determination of the *m*- in the presence of the *p*-isomer, the mixture in 0.1 *N* NaOH is neutralised with 0.1 *N* HCl. After the addition of saturated aq.  $\text{NaHCO}_3$  soln. and aq. Brentamine Fast Red (a stabilised diazotised 5-nitro-*o*-anisidine) the red colour is measured at 500  $\mu$ . The intensity of the colour given by the *p*-isomer is <2% of that given by the *m*-chlorophenol. The amount of the *p*-compound is determined by difference. J. N. ASHLEY

**5302. Spectral studies of halogenated benzaldehydes. I. Vibrational spectra of ortho-, meta- and para-chlorobenzaldehydes.** M. P. Padhye and B. G. Viladkar (Univ., Bombay, India). *J. Sci. Ind. Res., India, B*, 1960, **19** (2), 45-49.—Infra-red data of the compounds named are compared with those of benzaldehyde.

**5303. New reaction for the colorimetric micro-determination of phenacyl chloride.** A. Lamouroux and Y. Le Duigou. *Mém. Poudres*, 1958, **40**, 377-383 (in French).—Phenacyl chloride (I) can be determined by means of the yellow complex formed on heating with pyridine. The decomposition of the complex is prevented by the addition of piperidine. *Procedure*—To a soln. of the sample in dimethylformamide (3 ml, containing  $>75 \mu\text{g}$  of I) add pyridine (3 ml) and heat in a water bath for 3 min. Cool for 1 min. in running water and between 15 and 30 sec. later add piperidine (1 ml). Measure the extinction at 450  $\mu$  15 to 20 min. after the start of the determination. The method is suitable for the determination of I in the atmosphere with pyridine-dimethylformamide as the absorbent. W. T. CARTER

**5304. Application of a method for the measurement of solubility to the determination of water in cyclohexanone.** P. Aubertein. *Mém. Poudres*, 1958, **40**, 447-451 (in French).—*Procedure*—To the sample (100 ml) add paraffin wax (m.p. 52°) (3 g), heat to  $\approx 50^\circ$  and mix. Allow to cool slowly and note the temp. at which crystals appear. Read off the water content of the sample from a graph prepared with samples of known water content in the range 0.05 to 6% (w/w). The error is  $\pm 0.5\%$ . The

method is applicable to most solvents if a suitable solute is chosen. W. T. CARTER

**5305. Photometric determination of cyclohexanone oxime in the presence of caprolactam.** A. P. Terent'ev and M. Kosin'skii (M. V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 234-237.—When cyclohexanone oxime (I) is saturated with Cl, 1-chloro-1-nitrosocyclohexane (II) is quant. formed. Soln. of II obey Beer's law. When the method is used for the determination of I mixed with caprolactam the accuracy is within 2% of the oxime content. I (2 to 5 g) is dissolved in methanol (50 ml) and saturated with Cl. Simultaneously, 50 ml of methanol is chlorinated in a separate flask. The mixtures are diluted to 100 ml with methanol and their extinctions are measured and compared with standards. A. BURWOOD-SMITH

**5306. Note on the inverse isotope dilution analysis of salicylic acid.** C. E. Breckinridge, jun., and J. E. Christian (Bionucleonics Dept., Purdue Univ., Lafayette, Ind.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (5), 330.—Modifications of the method described previously (Swartz and Christian, *Anal. Abstr.*, 1959, **6**, 3045) extend the range to submilligram quantities. The wt. of 3:5-di-iodosalicylic acid crystals taken for radioactive counting is determined by measurement of the u.v. absorption at 328  $\mu$ , and a liquid scintillation counting technique is used with 0.4% of phosphor PPO and 0.01% of phosphor POPOP in toluene soln. As little as 1  $\mu\text{g}$  of salicylic acid can be determined with an average error of <16%. A. R. ROGERS

**5307. Reduction by borohydrides, in the presence of certain metals, of nitriles, and nitro or nitroso aromatic derivatives. Application to analysis.** M. Pesze and J.-F. Burtin. *Bull. Soc. Chim. France*, 1959, (11-12), 1996-1998.—Nitriles are reduced to primary amines in alkaline soln. in the presence of palladium salts, and aromatic nitro-compounds are reduced to primary amines in alkaline soln. in the presence of palladium or copper salts, and these amines can be determined colorimetrically. Phenols can be determined by reducing NN-dimethyl-*p*-nitroso-aniline with  $\text{BH}_4^-$  *in situ* to the amine, which forms a coloured quinone-imine with many phenols. *Procedure for nitriles*—The nitrile (50 to 200 mg) in 1 ml of ethanol is treated for 10 min. at room temp. with 1 ml of 0.2%  $\text{KBH}_4$  soln. in *N* NaOH and 0.5 ml of 0.05%  $\text{PdCl}_2$ . After acidification, neutralisation and making up to 5 ml, 6 ml of buffer soln. (phosphate-borate) is added and, at  $0^\circ$ , 1 ml of *p*-nitroaniline- $\text{NaNO}_2$  reagent. After making the soln. alkaline, the extinction is read at 500  $\mu$ . *Nitro-compounds (as Schiff's bases)*—The sample (*p*-nitrotoluene) is reduced as for the nitrile, but  $\text{CuSO}_4$  may be used instead of  $\text{PdCl}_2$ . After acidification to destroy  $\text{BH}_4^-$ , Schiff's bases are prepared by adding 2 ml of 0.5% *p*-dimethylamino-benzaldehyde or 3:3-diphenylacetaldehyde. After 15 min. extinctions are read at 440 or 400  $\mu$ , respectively. For *p*-nitrobenzoic acid a similar method is used, the amine being determined by diazotisation and coupling with 2-naphthol, giving an absorption at 485  $\mu$ , and for chloramphenicol by reduction and coupling with 4-aminosalicylic acid. *Phenols*—NN-Dimethyl-*p*-nitrosoaniline (0.15 g) in 2 ml of ethanol is made up to 100 ml with water, and 0.2 g of  $\text{KBH}_4$  and 2 ml of aq. 5%  $\text{CuSO}_4$  soln. are added. After 30 min. the soln. is filtered and adjusted to pH 1 to 2 with aq. 10% oxalic acid.

This reagent (0.5 ml) is added to the phenol sample in 5 ml of water, and, after 5 min., 3 ml of borate buffer (pH 9.8) and 0.5 ml of 1%  $K_4Fe(CN)_6$  soln. are added. After 5 min. the soln. is extracted with  $CHCl_3$ , and the extinction is measured at a wavelength suitable to the phenol. E. J. H. BIRCH

**5308. Gas partition chromatography of stereo-isomeric menthols.** H. J. Petrowitz, F. Nerdel and G. Ohloff (Org. Chem. Inst., Tech. Univ., Berlin). *J. Chromatography*, 1960, **3** (4), 351-358 (in German).—Mixtures of stereoisomeric menthols can be separated by gas partition chromatography with di-*n*-decyl phthalate as the stationary phase and helium as the carrier gas. Quantitative analysis of some mixtures of neomenthol and menthol, neomenthol and isomenthol, and menthol and isomenthol can be made with accuracies of  $\pm 1\%$ . Typical chromatograms are illustrated and retention times are given. G. P. COOK

**5309. Gas-chromatographic analysis of pyridine-nicotine mixtures.** R. Filleri and M. Vietti-Michelin (Univ. Turin, Italy). *Z. anal. Chem.*, 1960, **174** (3), 172-174 (in German).—Mixtures of pyridine and nicotine have been assayed with about  $\pm 2\%$  precision by gas chromatography on a Celite C22 column, impregnated with Apiezon L, operating at 200°, with N<sub>2</sub> as carrier gas. T. R. ANDREW

**5310. Selective spot test for isatin.** F. Feigl and D. Goldstein (Lab. da Prod. Mineral, Min. Agric., Rio de Janeiro, Brazil). *Talanta*, 1960, **4** (3), 209-210 (in English).—*Procedure*—Add ethanolic 4-nitrophenylhydrazine (I) soln. (1 drop) to the test material and heat for 5 to 10 min., then cool and add 1 drop each of 10% NaOH soln. and 1%  $Mg(NO_3)_2$  soln. A blue ppt. indicates isatin. For  $< 20 \mu g$  of isatin, extraction with ethyl ether is recommended to dissolve the excess of I. The limit of identification for isatin is 0.5  $\mu g$ . The reaction can also be used to detect  $Mg^{2+}$  or I ( $< 2 \mu g$ ). R. M. S. HALL

**5311. Simple method for the mercurimetric determination of thiophen.** M. Wroński (Inst. for Chem. Technol., Univ., Łódź, Poland). *Z. anal. Chem.*, 1960, **174** (4), 280-281 (in German).—The principle of the mercurimetric determination of allyl alcohol (*Anal. Abstr.*, 1960, **7**, 3304) has been applied to the determination of thiophen. *Procedure*—Dilute 5 to 20 ml of benzene containing 0.01 to 2% of thiophen with methanol, and mix 5 to 20 ml of this soln. with 2 to 5 ml of 0.1 N  $Hg(ClO_4)_2$  [100 ml of N  $Hg(ClO_4)_2$ , 25 ml of 60%  $HClO_4$  soln. and methanol to make 1 litre]. Boil under reflux for 1 to 4 min., stirring to prevent pptn. on the walls of the flask. Cool rapidly, add 1 ml of 2 N aq.  $NH_3$ , 25 to 40 ml of methanol and 1 ml of fresh thioflourescein soln. (0.02% in dil. aq.  $NH_3$ ), and titrate with 0.02 N thioglycolic acid (200 ml of N soln. diluted with 50% methanol to 1 litre) to a permanent blue colour. Titrate an aliquot of  $Hg(ClO_4)_2$  soln. similarly. Two equiv. of  $Hg^{2+}$  correspond to 1 mole of thiophen. The accuracy is within  $\pm 1\%$ . P. D. PARR-RICHARD

**5312. The mass-spectrometric hydrocarbon-type analysis of petrol.** G. Franke (B.P. Benzin u. Petroleum A.-G., Hamburg). *Erdöl u. Kohle*, 1960, **13** (4), 263-266.—The calculation of the % v/v of paraffins, cycloparaffins, dicycloparaffins and aromatics from mass-spectrometric data is illustrated for the simplest case, i.e., straight-run petrol with

no unsaturated component. The aromatics can be further analysed into structural types.

G. BURGER

**5313. Bromine number of petroleum distillates by electrometric titration.** A.S.T.M. A.S.T.M. Stand., Tentat. Stand., Suppl., 1959, Pt. 7, 80-88.—The specification has been revised.

REV. CURR. LIT. PAINT COL. VARN.

**5314. Sulphur in petroleum products, including liquefied petroleum gas, by lamp combustion.** A.S.T.M. A.S.T.M. Stand., Tentat. Stand., Suppl., 1959, Pt. 7, 89-106.—The method has been revised by the addition of an appendix permitting the determination of trace amounts of S by turbidimetric analysis.

REV. CURR. LIT. PAINT COL. VARN.

**5315. Apparatus for the determination of sulphur in petroleum products.** I. Ts. Lyast and A. D. Vshivtsev. USSR Pat. 125,940 (1.2.60).—Sulphur is determined by the amount of the soft  $\gamma$ -radiation from  $^{56}Fe$  absorbed by the sample; the residual radiation is measured on a Geiger-Müller counter in an apparatus in which the final current is proportional to the log. of the impulse rate; a scale indicates the sulphur content directly as a percentage. The apparatus and circuits are illustrated and described.

C. D. KOPKIN

**5316. Methods for the analysis and testing of coal and coke. Part 5. Gross calorific value of coal and coke.** British Standards Institution (2 Park St., London, W.1). B.S. 1016; Part 5: 1957. Amendment No. 1 (1.6.60).—Two corrigenda are published.

**5317. Determination of fluorine in coal. Adaptation of spectrophotometric methods.** G. E. McGowan (Baltimore Gas and Electric Co., Baltimore 3, Md., U.S.A.). *Fuel*, London, 1960, **39** (3), 245-252.—The ignited sample is washed into a flask and 5 ml of  $CuSO_4 \cdot 5H_2O$  soln. (20% w/v) is added. The soln. is reduced with zinc and NaOH soln., filtered and distilled with conc.  $H_2SO_4$ , and the distillate is collected. The pH is adjusted to 2.9 to 3.0, and thorium-alizarin indicator is added. The extinction is measured at 525 m $\mu$ , and the F content is read from a calibration curve. Results are within  $\pm 7.5$  p.p.m. in the range 0 to 300 p.p.m.

D. DE VOY

**5318. Use of the  $\pi$ -electron interaction for selective separation of some quinoline bases and aromatic and heterocyclic hydrocarbons from coal-tar distillates by gas-liquid chromatography.** J. Janák and M. Hřivnáč (Czech. Acad. Sci., Brno). *J. Chromatography*, 1960, **3** (4), 297-302 (in English).—Polyoxyalkylene adipate (Reoplex 400) is a satisfactory stationary phase for the selective separation of quinoline bases and unsaturated, aromatic and heterocyclic compounds having b.p. up to 300°. Retention data at 200° for a number of compounds, with Reoplex 400, Apiezon L and Silicon Elastomer E301 as stationary phases, are given, together with chromatograms showing their separation from coal-tar distillates. G. P. COOK

**5319. Standard methods of test for coke residue of creosote and distillation of creosote.** A.S.T.M. A.S.T.M. Stand., Tentat. Stand., Suppl., 1959, Pt. 6, 43-52.—The methods have been revised.

REV. CURR. LIT. PAINT COL. VARN.



**5320. Chromatographic separation of geraniol from linalol.** A. Castiglioni and R. Pilleri (Univ. Turin, Italy). *Z. anal. Chem.*, 1960, **174** (4), 278-279 (in German).—The chromatographic separation of alcohols is reviewed and the isolation of geraniol and linalol on paper is described. A 0.04-ml sample of a 4% ethereal or ethanolic soln. of the alcohols is spotted on to the paper and developed with a 4% aq. soln. of phenol for 8 to 10 hr. The dried strip is sprayed with a 1:9 mixture of phloroglucinol soln. (10% in 95% ethanol) and conc. HCl. Geraniol gives a brown fleck near the starting line, while linalol travels with the solvent front and gives a red-violet spot.

P. D. FARR-RICHARD

**5321. Determination of hexachlorophane in a dentifrice in the presence of methyl salicylate.** H. I. Achmeteli (Bristol-Myers Co., Hillside, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 278-280.—The residue remaining on evaporation of the acetone extract of the dentifrice is dissolved in water and the hexachlorophane is extracted with  $\text{CHCl}_3$ . An aliquot of this soln. is treated with a soln. of methylene blue and with a little 4-amino-phenazone soln. which, for a reason unknown, promotes rectilinearity of the concentration curve. The extinction of the  $\text{CHCl}_3$  layer is measured at 650 m $\mu$  and referred to a standard curve. Methyl salicylate does not interfere. Recoveries of 95-4 to 102.0% are reported.

A. A. ELDRIDGE

**5322. Paper chromatography of some certified dyes.** F. J. Bandelin and J. V. Tuschhoff (Flint, Eaton & Co., Decatur, Ill.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (5), 302-304.—The separation and identification of 5 to 50- $\mu\text{g}$  quantities of 20 dyes commonly used in pharmacy can be achieved, with few exceptions, by paper chromatography with 0.56% aq.  $\text{NH}_3$  containing 2% of isobutyl alcohol as solvent. Methods are given for the preliminary extraction and concentration of the dyes from tablets, powders and aq. soln.

A. R. ROGERS

**5323. Quantitative analysis of wool felts containing cellulose and casein fibres.** K. Korthum and M. Ashbrand. *Melliand Textilber.*, 1959, **40**, 193-196.—The disintegrated felt is extracted for 3 hr. with  $\text{CCl}_4$ , boiled twice with distilled water, and dried. To determine the cellulose content, the fibres (3 g) are boiled for 15 min. under reflux with 50 ml of 2% KOH, filtered through fritted glass, and rinsed. The fibres are treated for 15 min. at room temp. with hypochlorite soln. containing 50 g of active Cl per litre, filtered through fritted glass, rinsed with water and dil. acetic acid, and again with several washings of water. The residue, properly dried, consists of cellulose fibres. To correct for loss of cellulose during treatment, the fibre weight should be multiplied by 1.04. To determine the wool content, the fibres (3 g) are boiled with 300 ml of 0.2%  $\text{H}_2\text{SO}_4$  for 15 min., heated for a further 15 min. on a boiling-water bath, filtered through fritted glass, and washed with 1 litre of boiling water, followed by boiling with 1 litre of recently distilled water, and rinsing with 1 litre each of boiling and cold distilled water. The fibres are treated at 40° with 100 ml of water containing 1 g of trypsin and 0.3 g of  $\text{NaHCO}_3$  for 2 hr., filtered through fritted glass, washed with distilled water at 40° to 50°, with tap water, and finally with cold distilled water. The residue consists of wool and cellulose fibres. The wool content is the difference between this value and the cellulose value determined as

described above, and is corrected for loss during the determination by multiplying the result by 1.05. The casein content is the difference between the wool and cellulose fibre contents and 100. Proof of the correction factors is included.

CHEM. ABSTR.

**5324. Light-scattering methods for the chemical characterisation of polymers. A review.** F. W. Peaker (Univ., Birmingham, England). *Analyst*, 1960, **85**, 235-244.—The principles of turbidimetric titration are reviewed and a modification of the Spekker absorptiometer for use in the turbidimetric titration of high-polymer soln. is described. The phenomena of light scattering are discussed theoretically, and some applications and results are reviewed. (45 references.)

A. O. JONES

**5325. A three-component solvent system for quantitative separation of phenol-formaldehyde reaction products by ascending paper chromatography.** L. M. Yeddanapalli, A. K. Kuriakose and V. V. Gopalakrishna (Loyola Coll., Madras, India). *J. Sci. Ind. Res., India, B*, 1960, **19** (1), 25-27.—One-dimensional ascending paper partition chromatography on Whatman No. 1 paper with benzene-acetic acid-water (200:63:1) permits the complete separation, in  $\approx 8$  hr., of the following compounds in a mixture—2- and 4-hydroxymethylphenols; 2:4- and 2:6-dihydroxymethylphenols; 2:4:6-trihydroxymethylphenol; 2:2', 2:4' and 4:4'-dihydroxydiphenylmethanes; and 2':4'-dihydroxy-3-hydroxymethyldiphenylmethane. The spots are revealed by spraying first with a soln. of *p*-nitrophenyldiazonium fluoroborate in acetone and then with ethanolic KOH soln. Excellent separation, with well-defined circular spots, is attained, and a quant. determination of each component can be made by the spot-wt. method (Freeman, *Brit. Abstr. C*, 1953, 161) of the products from the acid- or alkali-catalysed phenol-formaldehyde reaction.

W. J. BAKER

**5326. Determination of hydroxymethyl groups in phenolic resins.** B. P. Ershov and A. S. Mosina (Sci. Res. and Design Inst. of Plastics, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (2), 243-244.—To a sample of the resin (100 to 200 mg) is added an 80% aq. soln. of phenol (1 ml) then 10 ml of *N* HCl through a reflux condenser. After 2 hr. on a water bath the unchanged phenol is distilled off and determined in the distillate. A control is carried out with 1 ml of 80% aq. phenol added to a known resin. The quantity of phenol used in the reaction is calculated on the assumption that 1 mol. of phenol reacts with one hydroxymethyl group.

A. BURWOOD-SMITH

**5327. Infra-red spectra of some methacrylic esters and their polymers.** G. Salomon, C. J. Schooneveldt-van der Kloes and J. H. L. Zwieters (Centr. Lab., T.N.O., Delft, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (4), 313-329.—Spectra of ten monomers and polymers of methacrylic esters and of methyl chloroacrylate have been studied between 6000 and 450  $\text{cm}^{-1}$ . The region 6000 to 1800  $\text{cm}^{-1}$  is occasionally valuable for quant. analysis.

N. E.

**5328. Determination of carboxyl groups in poly(ethylene terephthalate).** M. J. Maurice and F. Huizinga (N. V. Res. Lab., Arnhem, Netherlands). *Anal. Chim. Acta*, 1960, **22** (4), 363-368.—Errors due to thermal decomposition are avoided by

dissolving the sample (2 g) in 50 ml of a mixture of *o*-cresol (70 g) and  $\text{CHCl}_3$  (30 g) at a temp. of 90°. The cooled soln. is titrated potentiometrically with 0.1 N ethanolic KOH with the use of the glass electrode and the S.C.E. The method is compared with others in which different solvents are used and with visual or h.f. methods of titration.

H. N. S.

**5329. Complexometric determination of aluminium in poly(alumino-organosiloxane) resins.** Ya. I. Chulkov (V. I. Lenin All-Union Electro-tech. Inst.). *Zavod. Lab.*, 1960, **26** (4), 429-430.—The sample (0.3 to 0.4 g) is decomposed by wet combustion with  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , the soln. is diluted,  $\text{SiO}_2$  is removed, and an aliquot containing >20 mg of Al is treated with excess of EDTA soln. and neutralised to phenolphthalein with 5% aq.  $\text{NH}_3$ . After being boiled for 5 min. the hot soln. is treated with 2 ml of 2 N acetic acid and again boiled. The soln. at 40° is treated with 10 ml of an acetate buffer soln. (pH 6.0) and 1 ml of 0.8% haematoxylin soln. and diluted to 100 ml. The excess of EDTA is then titrated with 0.01 N  $\text{Al}^{3+}$  soln. to the colour change from yellow - green to pink. Interference is caused by Fe, Ti, Zn and Mn.

G. S. SMITH

**5330. Analysis of water emulsion paints.** M. Swann. *Paint J.*, 1960, **11**, 380-381, 392.—To determine the pigment content of emulsion paints the sample is dried in a thin film at room temp. and the binder is extracted by heating the film under reflux with a suitable solvent. For polyacrylic and poly(vinyl acetate) copolymers, benzene is suitable, but for styrene-butadiene copolymers *o*-dichlorobenzene is required. The pigment is separated by centrifuging and washing the extracted residue.

L. A. O'NEILL

**5331. Analysis of lead in a paint film.** E. Hoffmann (CSIRO, Melbourne). *Aust. Paint J.*, 1960, **4** (12), 23.—A method has been developed for detecting the presence of Pb in a paint film, without removing the film from the substrate, and deciding the extent to which the Pb may be responsible for sulphide staining. The Pb is extracted from the film by placing a filter-paper saturated with 2 N HCl or 7% EDTA (disodium salt) soln. in contact with it for 20 min., removing the paper, washing out the extract and determining the Pb colorimetrically as PbS. The extraction is not quantitative.

L. A. O'NEILL

**5332. Application of the photometric determination of methanol to the control of the production of terephthalate lacquers.** O. Mlejnek and H. Sečkářová (Res. Ind. of Insulators, Bratislava, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (4), 217-219.—Methanol must be first separated by steam-distillation. *Procedure*—Dilute 1 to 5 ml of the sample containing 1 to 5 mg of methanol to 10 ml with  $\text{H}_2\text{O}$ . Set aside for 10 min. at 35°, add  $\text{KMnO}_4$  soln. (3%) (2 ml) and set aside for another 10 min. at 35°. Then add oxalic acid (5%) (2 ml) and, after exactly 2 min., 5 ml of Schiff's reagent (dissolve 1 g of cryst. fuchsin in 1 litre of  $\text{H}_2\text{O}$ , add a soln. of 8 g of  $\text{NaHSO}_3$  in 25 ml of  $\text{H}_2\text{O}$  and remove the excess of  $\text{SO}_2$  by shaking in an open flask). Set aside for 1 hr. at 35°. Cool, dilute to 100 ml with  $\text{H}_2\text{O}$  and measure the extinction with a green filter (500 to 560  $\mu$ ). Compare with a calibration curve.

J. ŽÝKA

**5333. Quantitative determination of thiazole-type rubber accelerators by amperometric titration.** P. K. Chatterjee, D. Banerjee and A. K. Surcar

(Dept. Appl. Polymers, Indian Assoc. for the Cultivation of Science, Calcutta). *I.R.I. Trans.*, 1960, **36** (2), 65-69.—A method for the determination of 2-mercaptobenzothiazole (I) in the presence of Zn 2-mercaptobenzothiazole (II) and 2:2'-thio-bisbenzothiazole is described. Three samples are required if all the components are to be determined. The first is extracted with ethanol to recover the I and this is estimated by amperometric titration with 0.004 N  $\text{AgNO}_3$ . The second is acidified to convert II into I and the total I and II is titrated as I. The third is reduced with  $\text{SnCl}_2$  - HCl and the total thiazole is obtained by titration with 0.002 N  $\text{AgNO}_3$ .

J. L. PROSSER

**5334. The determination of chromium in aqueous solutions used in the tanning industry.** P. Spacu, E. Antonescu and I. Albescu (Lab. Inorg. Chem., Acad. R.P.R.). *Rev. Chim., Bucharest*, 1960, **11** (4), 230-231.—*Procedure*—The soln. containing organic compounds of Cr is evaporated to dryness on a water bath and repeatedly treated with 1 ml of conc.  $\text{H}_2\text{O}_2$  soln. and 1 ml of conc.  $\text{H}_2\text{SO}_4$  to complete destruction of organic matter. The acid soln. of  $\text{Cr}_2(\text{SO}_4)_3$  is diluted to 10 ml; the pH should be 4.5. To the hot soln. is added 0.15 g of solid  $\text{K}_2\text{SO}_4$ ; the soln. is cooled, and between 0.25 and 0.5 g of solid KSCN is added according to the amount of Cr present. In the presence of Fe, double the amount of KSCN is added. The soln. is warmed at 80° for 1 hr., and on cooling should be violet; if it is still green, add more KSCN and warm again. If Fe is present the cooled soln. is passed through a column of Wofatit P: only the  $[\text{Cr}(\text{SCN})_6]^{3-}$  is unchanged. The Fe can afterwards be eluted with 4 N HCl. The violet soln. of  $[\text{Cr}(\text{SCN})_6]^{3-}$  is diluted to 250 or 500 ml, and the colour is measured with a photometer at room temp., with water as blank. A standard curve is made with soln. of  $\text{Cr}_2(\text{SO}_4)_3$ . The method is thus suitable for the determination of Cr in the presence of organic acids, e.g., oxalic, formic, acetic, lactic or phthalic acid, or of Fe. The error varies from +0.85 to -3.24%.

H. SHER

**5335. Chemical determination of some explosives and explosive mixtures.** P. Aubertin and H. Pascal. *Mém. Poudres*, 1958, **40**, 113-125 (in French).—Explosive compounds containing the N- $\text{NO}_2$  group can be determined by titration in dimethylformamide with 0.1 N Na methoxide in benzene, with azo violet as indicator. The method gives accurate results with hexogen, which dissolves readily, but difficulties are experienced with samples containing wax. It is not applicable to materials containing pentaerythritol, toluite and nitroguanidine. Nitric acid esters can be analysed by the procedure of Fréjacques and Leclercq (*Ibid.*, 1956, **38**, 39). The sample is dissolved in conc.  $\text{H}_2\text{SO}_4$ , hydrolysis takes place and the liberated nitric acid is determined by titration with standard  $\text{FeSO}_4$  soln. This method gives good results with pentaerythritol, tetryl, nitroguanidine and dipentaerythritol hexanitrate, but is not applicable to hexogen, which is destroyed by conc.  $\text{H}_2\text{SO}_4$ . The rate of dissolution of the sample depends on the concn. of the  $\text{H}_2\text{SO}_4$ ; it is possible to employ 92 to 93%  $\text{H}_2\text{SO}_4$  by heating under reflux at 50° to 60°. Nitroguanidine is hydrolysed only slowly by conc.  $\text{H}_2\text{SO}_4$ , but may be analysed by adding an excess of standard  $\text{FeSO}_4$  soln., stirring for 1 hr. and back-titrating with 1%  $\text{HNO}_3$ .

W. T. CARTER

**5336. Analysis of explosives in non-aqueous media. Determination of potassium salts.** L. Marvillet and J. Tranchant. *Mém. Poudres*, 1959,

**41.** 171-177 (in French).—Potassium nitrate and sulphate and potassium aluminium fluoride in acetic acid soln. can be titrated with 0.1 N  $\text{HClO}_4$  in glacial acetic acid. The end-point is detected potentiometrically with glass and silver-silver chloride electrodes; for  $\text{K}_2\text{SO}_4$  a visual end-point is possible, with crystal violet as indicator. To avoid the separation of the potassium salts, the soln. is heated to 70° to 80° during the titration. Potassium nitrate can also be determined by dissolving the sample or the ignited residue in acetic acid and titrating directly with 0.1 N  $\text{HClO}_4$ . For samples containing 1% of potassium salts the precision is  $\pm 3\%$ .  
W. T. CARTER

**5337. Determination of butyl phthalate in nitro-cellulose granules.** L. Marvillet and J. Tranchant. *Mém. Poudres*, 1959, **41**, 179-182 (in French).—*Procedure*—Extract the sample (5 g) with dichloromethane for 4 hr. Evaporate off most of the dichloromethane, add ethyl ether (5 ml) and continue the evaporation until all solvent is removed. Add 4% ethanolic KOH soln. (50 ml) and boil under reflux for 1.5 hr. Filter through a G4 sintered-glass filter, wash the ppt. with ethanol-ethyl ether (1:1) (100 ml), dry it for 0.5 hr. at 60° then for 1 hr. at 150° and weigh. Esters of nitric acid and nitro derivatives must be absent, but stabilisers do not interfere.  
W. T. CARTER

**5338. Staining of cast high explosives for observation of the crystalline structure.** H. J. Yallop (Armament Res. and Devel. Estab., Fort Halstead, Kent, England). *Analyst*, 1960, **85**, 300-301.—The staining technique is based upon the coloured complexes formed between some nitro compounds and dimethylaniline, which gives a red colour with TNT, orange with tetryl and picric acid, and no colour with the other common high explosives. One face of a section of the explosive ( $\approx 3$  mm thick) is smoothed with glass-paper. The section is then glued by this face to a microscope slide and its thickness is reduced to  $\approx 1$  mm with a microtome. The surface is lightly wiped first with a cotton wool pad moistened with acetone and then with one moistened with dimethylaniline. The specimen is then examined microscopically by transmitted white light. Typical photomicrographs are shown with an interpretation of their appearance.  
A. O. JONES

See also Abstracts—5133, Determination of EDTA. 5139, Oxidation of org. products with  $\text{HIO}_4$ . 5163, Reducing power of zinc dust. 5240, Determination of F in org. compounds. 5425, Aldehydes and ketones in volatile oils.

#### 4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

##### Biological fluids, animal and vegetable tissues

**5339. Rapid sensitive method for determining  $^3\text{H}$ -water in body fluids by liquid scintillation spectrometry.** H. Werbin, I. L. Chaikoff and M. R. Imada (Dept. Physiol., Univ. of California, Berkeley). *Proc. Soc. Exp. Biol. Med.*, 1959, **102** (1), 8-12.—The method is based on distillation of body fluids with benzene to produce an almost pure sample of  $^3\text{H}$ -water and the use of the solvent

naphthalene-dioxan (1.5 g:12 ml) to transfer the excitation energy of  $^3\text{H}$  to the phosphors, 2:5-diphenyloxazole and 1:4-di-(5-phenyloxazol-2-yl)-benzene. The determination of  $^3\text{H}$  in urine and plasma gave recoveries ranging from 98 to 104%.  
N. E.

**5340. New tonometric method for the determination of dissolved oxygen and carbon dioxide in small samples.** J. D. Jones (Univ., Sheffield, England). *J. Exp. Biol.*, 1959, **36**, 177-190.—A micro-method, in which a small gas bubble is equilibrated with the sample and subsequently analysed, is described whereby tensions of  $\text{CO}_2$ , O and N can be determined in fluid samples of 0.5-ml or less, in 20 to 25 min. Duplicate determinations of the tensions of  $\text{CO}_2$ , O and N gave max. coeff. of variation of 3.0, 2.2 and 1.2%, respectively. A comparison of the method with the Winkler micro-method gave a mean difference of 3%.  
CHEM. ABSTR.

**5341. Sensitive procedure for determining carbon monoxide in blood or tissue utilising gas-solid chromatography.** A. M. Dominguez, H. E. Christensen, L. R. Goldbaum and V. A. Stembridge (Armed Forces Inst. of Pathol., Washington, D.C.). *Tox. Appl. Pharmacol.*, 1959, **1**, 135-143.—The method is rapid and simple and the error ranges from  $<5\%$  to  $\approx 10\%$  for blood samples containing  $>10\%$  or  $<10\%$ , respectively, of carboxyhaemoglobin. Methane, ethane,  $\text{H}_2\text{S}$ , acetylene, H, Ar,  $\text{CO}_2$  and products of putrefaction do not interfere.  
CHEM. ABSTR.

**5342. The determination of metals in blood serum by atomic absorption spectroscopy. III. Sodium and potassium.** J. B. Willis (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Lab., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (5), 551-558.—Results obtained on small samples ( $<0.1$  ml) compared with those obtained by flame photometry showed an agreement within  $\pm 2.5\%$  when nine samples, each containing  $\approx 300$  mg of Na per 100 ml, were examined. The effects obtained by variations in technique are discussed and are compared with those of flame photometry.  
E. G. CUMMINS

**5343. Studies in serum electrolytes. XXII. Rapid, reliable method for serum potassium using tetraphenylboron.** F. W. Sunderman, jun., and F. W. Sunderman (Div. of Metab. Res., Jefferson Med. Coll., Philadelphia, Pa.). *Amer. J. Clin. Path.*, 1958, **29** (1), 95-103.—The ppt. formed by the interaction of  $\text{K}^+$  with Na tetraphenylboron is stabilised by the addition of gum ghatti. After 15 min. the extinction of the reaction mixture is measured at 420 m $\mu$ . A modification that requires only 0.2 ml of serum is described. The results of this rapid and simple method are in good agreement with those of other methods.  
P. NICHOLLS

**5344. Determination of serum copper and iron in a single small sample.** J. W. Landers and B. Zak (Wayne State Univ. Coll. of Med., Mich., U.S.A.). *Amer. J. Clin. Path.*, 1958, **29** (6), 590-592.—The complexing agents for Fe and Cu, 4:7-diphenyl-1:10-phenanthroline and 2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline, respectively, are converted into their water-soluble sulphonated derivatives by treatment with chlorosulphonic acid. This obviates the necessity of extracting the metals into an organic phase. The buffered soln. of the reagents are separately added to aliquots of serum filtrate prepared from 1.0 ml of serum. Stoichiometric

coloured complexes are formed instantaneously and can be measured. These reactions are specific and sensitive.

P. NICHOLLS

**5345. Flame-spectrophotometric determination of strontium and calcium in bone.** A. Schmid and K. Zipf (Tierärz. Fac., Univ., München, Germany). *Biochem. Z.*, 1959, **331**, 144-149.—The powdered bone-ash (15 mg) is dissolved in  $N$  HCl (1 ml), and diluted to 150 to 200 ml with water; the pH is brought to 7.0 with 0.1  $N$  aq.  $NH_3$ . The addition (dropwise) of  $FeCl_3$  soln. (0.5 mg per ml) (1 ml) and ammonium acetate buffer (1 milli-equiv. of acetic acid and 0.5 milli-equiv. of aq.  $NH_3$  per ml) (1 ml) is followed by a short boiling, cooling and dilution to 300 ml. After filtration from the phosphate, Ca and Sr are determined flame-spectrophotometrically.

N. E.

**5346. Micro-determination of mercury in biological media of animal origin.** R. Truhaut and C. Boudène (Lab. de Toxic. et d'Hyg. Ind., Fac. de Pharm., Paris, France). *Bull. Soc. Chim. France*, 1959, (11-12), 1850-1854.—A method is described for the determination of Hg in biological media other than urine.

(i) *Mineralisation*—The sample of blood (10 to 20 g) or organs (2 to 5 g) is weighed and heated gently under reflux (apparatus described) with 5 ml of  $H_2SO_4$  until proteins are destroyed. Conc.  $H_2O_2$  is added through the condenser, 1 ml at a time, until the material is decolorised. The contents of the flask are then distilled into 10 ml of satd.  $KMnO_4$  soln. and  $H_2SO_4$  (10% w/w) (equal vol.) until fumes of  $SO_3$  appear in the distilling flask. After cooling, 1 ml of  $HNO_3$  at a time is added with gentle heating until a light-yellow liquid is obtained. After heating for 30 min. the contents of the receiver are treated with 1 g of  $KMnO_4$  and the mixture is heated under reflux for 1 hr. The liquid is cooled and enough satd. hydroxyammonium chloride soln. is added to decolorise it, and, after boiling, the liquid is treated with 4 ml of 10% urea soln. and the pH is adjusted to 2 with 50% Na acetate soln. (ii) *Separation of Hg*—The liquid is extracted several times with 1-ml portions of di-2-naphthylthiocarbazon (0.0025% in  $CHCl_3$ ) (I) and to the extract are added 4 ml of 15% aq.  $H_2SO_4$  and 2 drops of satd.  $KMnO_4$  soln. After removal of the org. layer, the aq. liquid is washed with light petroleum (5 ml), 1 ml of satd.  $KMnO_4$  soln. is added to the acid soln. and, after heating for 30 min. under reflux, 3.5 ml of  $H_2SO_4$  is added. After heating again under reflux for 15 min. the soln. is transferred to a water-entrainment apparatus (described) and 4 ml of 10%  $SnSO_4$  suspension in 1%  $H_2SO_4$  is added. The Hg and water are distilled over together by means of an air condenser into a micro-Kjeldahl flask containing  $H_2SO_4$ - $KMnO_4$  soln. (iii) *Titration*—To this flask and a blank containing an equal vol. of  $H_2SO_4$ - $KMnO_4$  soln. are added 1 ml of satd. hydroxyammonium chloride soln. I soln. is then added, 0.5 ml at a time, to the flask until the  $CHCl_3$  layer is lilac mauve, and exactly the same quantity of I is added to the blank. The blank is then titrated with a standard soln. of Hg (67.7 mg of  $HgCl_2$  in 1 litre of 5% HCl) until the colour is the same.

E. J. H. BIRCH

**5347. Studies on inorganic components in biological materials. XIII. Determination of thallium.** Hiroshi Hamaguchi, Naichi Ota and Kazuhiko Kawasaki (Fac. Sci., Univ. of Educ., Koishikawa, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1428-1432.—When Tl is determined

photometrically by the iodine method (Haddock, *Analyst*, 1935, **60**, 394) the results are higher than those obtained by other procedures (Onishi, *Anal. Abstr.*, 1958, **5**, 2141; Woolley, *Analyst*, 1958, **83**, 477). This appears to be due to the formation of peroxides on treatment of the dithizone extract with  $H_2O_2$  or  $(NH_4)_2S_2O_8$ . A modified method is proposed in which Tl is extracted with dil.  $HNO_3$  from a  $CHCl_3$  soln. of Tl dithizonate. The iodine method can then be used.

K. SAITO

**5348. Spectrophotometric determination of traces of tin in biological and other materials.** W. Oelschläger (Inst. für Tierernährungslehre der Landwirtschaft. Hochsch., Hohenheim, Germany). *Z. anal. Chem.*, 1960, **174** (4), 241-254 (in German).—The merits of toluene-3:4-dithiol and phenyl-fluorone (I) as reagents for Sn are compared; I is less affected by interfering ions. Tin is separated from Mo by pptn. with  $PO_4^{3-}$ ; W interferes also, but is unlikely to be present. *Procedure*—Ash 30 to 40 g of material at  $450^\circ$  to  $500^\circ$  in a closed muffle-furnace overnight. Dissolve the residue in 6  $N$  HCl (20 ml), cover and heat at  $100^\circ$  for 15 min. Add  $H_2O$  (30 ml) and filter into a 100-ml flask. Ash the washed paper at  $450^\circ$ , dissolve the residue in 6  $N$  HCl (10 ml) and warm; add  $H_2O$  (20 ml) and filter. Remove any  $SiO_2$  in the residue with HF, evaporate with conc. HCl, dilute and filter. Combine all the filtrates and make up to 100 ml. Pipette 50 ml into a centrifuge tube, add 2%  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3$  soln. (2 ml) and 5%  $(NH_4)_2HPO_4$  soln. (1 ml). Add conc. aq.  $NH_3$  until the soln. is cloudy, clear with 2  $N$  HCl, then adjust the pH to between 4 and 5 with Na acetate. Heat at  $100^\circ$  for 20 min., centrifuge for 20 min. and decant the supernatant liquid. Wash the ppt. with hot 1% Na acetate soln. (20 ml), then dissolve it in 6  $N$  HCl (2 ml) and dilute the soln. to 25 ml. Add 10% KSCN soln. (5 ml) and ascorbic acid until a pale-pink colour remains. Add ethyl acetate (20 ml), shake for 1 min. and repeat with a further 10 ml ( $\times 2$ ). Evaporate the organic phases to dryness and dissolve the residue in conc.  $H_2SO_4$  (1 ml). Add 30%  $H_2O_2$  soln. (20 drops), cover and heat at  $120^\circ$  for 30 min. Add 0.1 g of hydroxyammonium sulphate and heat again for 30 min. Add 5 ml of a 0.03% soln. of I and dilute to 25 ml; read the extinction 2 hr. later at 500  $m\mu$ . Use the same amounts of  $H_2SO_4$  and hydroxylamine for the standard soln. (0 to 20  $\mu g$  of Sn). *Preparation of I soln.*—Add 10 ml of 2% NaOH soln. to 60 mg of I and shake for  $> 1$  min.; add 1 ml of conc.  $H_2SO_4$  and dilute with 1.5% Na lauryl sulphate soln. to 200 ml.

P. D. PARR-RICHARD

**5349. Use of oscillography in quantitative analysis. Determination of lead in blood.** O. Rottová-Kloubková and R. Kalvoda (Dept. Anal. Chem., Charles' Univ., Prague). *Pracovní Lékařství*, 1960, **12** (1), 20-23.—The method is based on the preliminary electrolytic concentration of Pb at a mercury electrode (Kalvoda, *Chem. Listy*, 1957, **51**, 696). The results were evaluated with the use of Cd as internal standard, because the cut-ins of Pb and Cd are well separated and the ratio of their depths is constant. *Procedure*—To Na citrate soln. (3.8%) (2 ml) add the blood sample (8 ml) and HCl (8%) (12 ml), mix thoroughly and heat on a water bath for 5 min. Cool, add  $H_2O$ , filter through paper, divide the filtrate into two portions and electrolyse for 5 min. (at 25 mA). Wash the electrodes with 0.02  $M$   $H_2SO_4$ , transfer them into a mixture of 0.5  $M$   $KClO_4$  and 0.2  $M$   $H_2SO_4$  and



continue the electrolysis for 2 min. Then switch the electrodes to the oscilloscope and register the anodic cut-in of the polarographic curve. Carry out a reagent blank. To a second sample add Cd and adjust the concn. of  $\text{Cd}^{2+}$  to  $5 \times 10^{-4} M$ ; to the third and next samples add  $\text{Pb}^{2+}$  to a concn. of  $10^{-4} M$  to  $10^{-5} M$ . Register and measure the cut-ins of Pb and Cd, compare with the calibration curve and evaluate the results. The described procedure has a greater sensitivity than recording the polarogram. J. ZYKA

**5350. Photometric determination of phosphorus in serum by means of the molybdovanadate method.** W. Boguth and V. Horn (Veterinary Physiological Inst., Justus Liebig Univ., Giessen, Germany). *Biochem. Z.*, 1959, **332**, 74-76.—Phosphorus is determined by ignition with  $\text{Mg}(\text{NO}_3)_2$  and spectrophotometry of the molybdovanadophosphoric acid complex. N. E.

**5351. Colorimetric determination of phosphoric acid in plant materials by a molybdovanadate method.** M. Koter and H. Panak (School of Agric., Olsztyn, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 317-324.—In the method described, ammonium metavanadate and molybdate are used. The addition of 2 ml of 60%  $\text{HClO}_4$  has no influence on the results, but the addition of more acid causes an increasing error, especially if the extinction is measured after prolonged standing of the soln. Results for 40 samples of plant material agreed with those by the gravimetric Lorenz method. L. SMAKOWSKI

**5352. Analytical chemistry of trace elements and mineral constituents in biological materials. XIX. Utilisation of rubenic acid [dithio-oxamide] in the determination of copper in plant ash by polarography.** Katsumi Yamamoto (Tohoku Univ., Sendai). *Sci. Rep. Tohoku Univ., Ser. I*, 1958, **42**, 196-201 (in English).—To the HCl soln. of the plant ash is added citric acid, NaOH to a pH of 8, and a 0.5% soln. of dithio-oxamide in ethanol. The soln. is allowed to stand overnight and the ppt. is centrifuged, washed with  $\text{NH}_4\text{Cl}$  soln. and wet-ashed. The soln. is evaporated to dryness and the Cu is extracted with HCl and determined polarographically by the standard addition method, with a supporting electrolyte of aq.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ . The variation is  $\pm 10\%$ .

**XX. Determination of zinc and copper in plant ash by an oscillographic method.** Katsumi Yamamoto. *Ibid.*, 1958, **42**, 202-208.—The plant ash is dissolved in HCl and extracted with a  $\text{CCl}_4$  soln. of dithionite in the presence of Na citrate. The Zn dithionite is washed with water and extracted with 0.02 N HCl. The Cu dithionite is wet-ashed and dissolved in HCl. The Zn and Cu are determined separately by the oscillographic technique, with a supporting electrolyte of aq.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  soln. The method is not applicable below  $10^{-4} M$  for either metal. Variation for both metals was  $\pm 3$  to 5%. CHEM. ABSTR.

**5353. Diagnostic composition [for the detection and estimation of glucose and other reducing sugars in blood].** Miles Laboratories, Inc. [Inventor: A. H. Free]. Brit. Pat. 843,221; date appl. 23.10.57. Addition to Brit. Pat. 808,742 dated 17.5.56.—The composition comprises glucose oxidase (25 to 500 parts), peroxidase (1 to 100 parts), a compound which undergoes a colour reaction in the presence of hydrogen peroxide (e.g., o-tolidine hydrochloride)

(20 to 200 parts), a solid buffer (anhyd. citric acid-Na citrate dihydrate) (8:17) (200 parts), and a protein degradation product (e.g., gelatin) to serve as a stabiliser (up to 1000 parts). (Cf. *Anal. Abstr.*, 1959, **6**, 3099.) J. M. JACOBS

**5354. Solvent for quantitative and qualitative determination of sugars using paper chromatography.** P. Colombo, D. Corbetta, A. Pirotta, G. Ruffini and A. Sartori (Vita Mayer & Co., Milan, Italy). *J. Chromatography*, 1960, **3** (4), 343-350 (in English).—A solvent mixture of ethyl acetate, pyridine and water (3:6:1; 1:15) gave satisfactory separation of the principal monosaccharide constituents of the carbohydrate fraction of wood, viz. glucose, galactose, mannose, arabinose and xylose. The spots were detected after elution and drying of the chromatogram by a modified Partridge reagent consisting of 2.5% of aniline acid phthalate in water-satd. butanol. Quantitative measurement of the spots was carried out with a photo-electric densitometer. The coeff. of variation ranged from  $\pm 5\%$  for arabinose to  $\pm 12.6\%$  for xylose at a level of 7.5 mg per ml for xylose and  $\approx 2.5$  mg per ml for the other sugars. G. P. COOK

**5355. Sensitive method for detecting sugars on paper chromatograms.** J. K. Roy (Dept. of Anthropology, Gov. of India, Indian Museum, Calcutta). *Analyst*, 1960, **85**, 294-295.—An aliquot (0.002 ml) of a 0.2% soln. of each sugar is placed on chromatographic paper and the chromatogram is developed with ethyl acetate-acetic acid- $\text{H}_2\text{O}$  (3:1:3) as descending solvent. The paper is dried in an air current at  $30^\circ$ , sprayed with a 1% soln. of  $p$ -aminobenzoic acid in isobutyl alcohol, and immediately heated at  $105^\circ$  for  $\approx 10$  min. The paper is then sprayed with a 0.5% soln. of oxalic acid in glacial acetic acid. A mixture of 2- $\mu$ g amounts of raffinose, glucose, xylose and rhamnose gave detectable spots. With 4- $\mu$ g amounts of glucose, mannose, xylose and rhamnose all the spots were distinct. A. O. JONES

**5356. Determination of ketone bodies in blood.** R. L. Reid (C.S.I.R.O., Sheep Biology Lab., Prospect, N.S.W., Australia). *Analyst*, 1960, **85**, 265-271.—A suitably diluted protein-free filtrate from whole blood is gradually added from a dropping-funnel to 8 ml of 7 N  $\text{H}_2\text{SO}_4$  already boiling in a specially designed distillation apparatus. The distillate (5 ml) contains pre-formed acetone together with acetone formed by decarboxylation of acetoacetic acid. A soln. of  $\text{K}_2\text{Cr}_2\text{O}_7$  is run in through the dropping-funnel and distillation is continued into another receiver. The distillates are adjusted to 5 ml, and 10 N NaOH (2 ml) and 2 ml of an ethanolic soln. of salicylaldehyde are added. The liquid is vigorously shaken and heated in a water bath at  $\approx 55^\circ$  for 20 min., and after 1 hr. the extinction is measured at 530  $m\mu$  against a reagent blank with water in place of the sample, the result being compared with those obtained with standard soln. of acetone. For each ketone fraction the standard deviation of a single determination is  $< \pm 0.15$  mg per 100 ml of blood at levels below 3 mg per 100 ml. A. O. JONES

**5357. Purification and identification of flavanone glycosides in the peel of the sweet orange.** W. J. Dunlap and S. H. Wender (Oklahoma Univ., Norman, U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (2), 228-231.—A description is given of the preparation of sample extracts and the separation

of isosakuranetin 7-rhamnoglucoside, naringin and hesperidin on columns of Magnesol developed with water-saturated ethyl acetate. The three main components are identified by u.v. spectroscopy and by paper chromatography before and after hydrolysis. W. H. C. SHAW

**5358. Gravimetric determination of hesperidin.** A. Kwietny and G. Zimmermann (Israel Inst. of Technol., Haifa). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 235-237.—The loss of hesperidin suffered in the gravimetric method of determination increases with the time during which the hesperidin is kept in alkaline solution before acidification and evaporation. The loss can be reduced to 5% by dissolving the crude hesperidin in alkaline methanol under vacuum in an ice bath, keeping for 1 hr., and adjusting the pH to 6.5 with  $NH_4Cl$  before evaporation. A. L. ELDRIDGE

**5359. The identification, by chromatography, of plant phenolic acids.** R. K. Ibrahim and G. H. N. Towers (McGill Univ., Montreal, Canada). *Arch. Biochem. Biophys.*, 1960, **87** (1), 125-128.—Descending chromatography is carried out on Whatman No. 1 paper developed (without equilibration) in the first dimension with the upper phase from benzene-acetic acid-water (6:7:3). After drying, development in the second dimension is with a mixture of sodium formate-formic acid-water (10:1:200). The air-dry chromatograms are then examined under u.v. light or sprayed with 1%  $FeCl_3$  soln., diazotised  $p$ -nitroaniline or diazotised sulphonic acid. The chromatographic behaviour of 21 common phenolic acids is depicted and their behaviour with the spray reagents is tabulated. The phenolic acids found in 10 plants are listed. W. H. C. SHAW

**5360. Micro-titration of total fatty acids of serum, with notes on the estimation of triglycerides.** M. J. Albrink (Yale Univ., U.S.A.). *J. Lipid Res.*, 1959, **1**, 53-59.—Duplicate determinations of total serum fatty acids, cholesterol, lipid P, and triglycerides by difference, are possible by this method by using 1 ml of the specimen. Essential steps are the extraction of the lipids, saponification, extraction, and micro-titration of the liberated fatty acids. Recoveries of pure fatty acids were 97%. Short-chain fatty acids and intermediates of carbohydrate metabolism were not detected by this procedure.

CHEM. ABSTR.

**5361. Paper-chromatographic separation of phosphatides.** I. L. Hörhammer, H. Wagner and G. Richter (Inst. Pharm. Arzneimitt., Univ., München, Germany). *Biochem. Z.*, 1959, **331**, 155-161.—By the use of formaldehyde-treated paper and  $n$ -butanol-acetic acid-water (4:1:5) as solvent, crude phosphatide mixtures can be reproducibly separated. N. E.

**5362. Total, phospholipid and labile phosphorus in serum employing chloric acid and 4-aminodiphenylamine.** J. F. Goodwin (Wayne State Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1959, **100**, 217-219.—An improvement in the  $HClO_4$  procedure previously reported (Goodwin *et al.*, *Anal. Chem.*, 1958, **30**, 1097) is described. The use of  $p$ -semidine (4-aminodiphenylamine hydrochloride) as a reducing agent in the molybdenum blue method was found to give a stable colour in the presence of the neutralised decomposition products of  $HClO_4$  digestion. N. E.

**5363. Hydrolytic procedure for the identification and estimation of individual phospholipids in biological samples.** R. M. C. Dawson (Inst. of Animal Physiol., Babraham, Cambridge, England). *Biochem. J.*, 1960, **75** (1), 45-53.—The phospholipids formed by selective hydrolytic degradation are separated by paper chromatography, and their phosphorus contents are measured by a standard method. From the these results, the nature and amounts of the phospholipids originally present are inferred; appropriate corrections are based on the hydrolysis of reference compounds. An alkaline hydrolysis is first carried out; the alkali-stable phospholipids are then subjected to mild acid hydrolysis, when the deacylated plasmalogens break down into a long-chain aldehyde and their corresponding water-sol. phosphodiester. The residual phospholipids are hydrolysed with methanolic  $HCl$ , when sphingomyelin gives phosphorylcholine and sphingosylphosphorylcholine. Samples of the three hydrolysates are separated on filter-paper. The P-containing spots are located by an acid molybdate spray, followed by irradiation with u.v. light. The spots are then cut out and ashed with  $HClO_4$ , and the P is determined colorimetrically by the molybdate method. The disadvantages of other methods of determination of phospholipids are enumerated. The present method requires only one assay, for P, and complex lipid samples can be resolved and assayed in two days. J. N. ASHLEY

**5364. Chromatography of the phospholipids of rabbit skin.** H. P. Schwarz, L. Dreisbach, R. Stambaugh, A. Kleschick and M. Barrionuevo (Philadelphia Gen. Hosp., Pa., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (2), 171-178.—Extracts of the prepared skin samples are chromatographed on silicic acid columns which are eluted for 8 hr. with  $CHCl_3$ -methanol mixtures graded to undiluted methanol. Residues obtained by evaporation of the various fractions are then examined by i.r. spectrophotometry, by chromatography on silicic acid-impregnated Whatman No. 1 paper developed with diisobutyl ketone-acetic acid-water (8:5:3), and by the use of various chemical methods. Recovery of total lipid P is 91%. The separations attainable, the significance of the results and the proportions of the phospholipid fractions obtained are given and discussed. W. H. C. SHAW

**5365. Quantitative glass-(fibre)paper chromatography: phosphatidylcholine and sphingomyelin.** J. E. Muldrey, jun., N. Miller and J. G. Hamilton (Tulane Univ., New Orleans, La., U.S.A.). *J. Lipid Res.*, 1959, **1**, 48-52.—A rapid chromatographic procedure was developed for the separation of sphingomyelin, phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol and free fatty acids on glass-fibre paper coated with sodium silicate. The phosphatidylcholine and sphingomyelin were quant. determined by densitometry of the charred chromatogram, which was obtained by spraying the strip with  $H_2SO_4$  and heating in an oven. Separation of phosphatides on sodium silicate treated glass-fibre paper is more rapid than on silicic acid-impregnated paper, and the former is easier to prepare. CHEM. ABSTR.

**5366. Isolation and determination methods for brain cerebrosides, hydroxy fatty acids and unsaturated and saturated fatty acids.** Yasuo Kishimoto and N. S. Radin (Med. School, Northwestern Univ., Chicago). *J. Lipid Res.*, 1959, **1**, 72-78.—A new

method is described for the isolation of nearly pure total cerebrosides from fresh brain. Florisil columns are used to separate the cerebroside hydroxy and normal acids, in the form of their esters, and to separate the saturated and unsaturated esters of each group. The esters within each class are determined by gas chromatography, the hydroxy esters being run as the methyl ethers. Yields in the various steps are close to the theoretical. Lower homologues were detected in all four classes of rat-brain cerebroside acids. Particularly large amounts of  $C_{22}$  and  $C_{24}$  saturated acids were found.

CHEM. ABSTR.

**5367. Use of N-ethylmaleimide for the colorimetric determination of amino acids.** Z. Peizker (Inst. Hyg. and Ind. Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (5), 1514-1516 (in German).—Carboxyditiothiocarbamic acids formed by the reaction of amino acids with  $CS_2$  yield a red colour with N-ethylmaleimide in an alkaline medium, in the presence of cyanide. *Procedure*—To the soln. of the sample (0.5 ml) add 0.07 M  $Na_2B_4O_7$  (0.5 ml),  $CS_2$  soln. (1% in acetone) (1 ml) and set aside for 30 min. Add 0.07 M  $Na_2B_4O_7$  (2 ml), remove the excess of  $CS_2$  by a 3-min. bubbling with  $N_2$ , add KCN soln. (5%) (0.2 ml) and make up to 5 ml. To 0.5 ml of this soln. add  $H_2O$  (0.5 ml), 0.1 M ethylmaleimide (1 ml) and ethanolic KCN soln. (5 g of KCN and 5 g of NaCN in 65 ml of  $H_2O$ , plus 25 ml of ethanol) (0.2 ml). After 1 hr. measure the extinction at 510 m $\mu$  against a blank. The procedure is suitable for the determination of 5 to 500  $\mu$ g of amino acids per ml of sample; Cu and Hg, which form stable complexes with carboxyditiothiocarbamic acids, interfere. Extinction coeff. are listed for 22 amino acids.

J. ŽYKA

**5368. Determination of amino acids. II. Effect of time of hydrolysis of protein on the determination of amino acids.** N. Matsuno, A. Nishihara and S. Isobe. *Ann. Rep. Nat. Inst. Nutr., Tokyo*, 1959, **42-44** (in English).—Figures are given for the amounts of amino acids obtained from casein, egg albumin, gelatin, zein and fish meal, after hydrolysis with 4 N HCl for 2, 4, 6, 8, 10 and 12 hr. Methionine, threonine, and isoleucine gave the highest yields at 6 hr.; lysine and leucine at 6 hr. for all proteins except fish meal, for which yields were highest at 8 hr.; phenylalanine at 6 hr. for gelatin, zein and fish meal, and 8 hr. for casein and egg albumin; and valine at 6 hr. for casein and egg albumin, and 8 hr. for gelatin. The addition of 3 parts of starch to 1 part of protein diminished the yields of the amino acids; 10 parts of starch gave a greater loss.

**III. The hydrolysis time and effect of carbohydrate on tryptophan determination.** S. Isobe. *Ibid.*, 1959, **45-46**.—Casein and albumin were hydrolysed with 4 N NaOH at 121° (i) alone, (ii) with cysteine, (iii) under  $CO_2$ , (iv) with cysteine and under  $CO_2$ , (v) with glucose, and (vi) with starch, and tryptophan was determined in the hydrolysate at 10, 12, 14 and 16 hr. Yields of tryptophan from albumin were increased in the presence of cysteine, and decreased in the presence of carbohydrate; the effects of carbohydrate on the yields from casein were slight, but a considerable loss was found with albumin.

M. D. ANDERSON

**5369. Determination of lysine in protein hydrolysates using lysine decarboxylase from *Salmonella hadar*.** Y. Kott and N. Lichtenstein (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1960, **22** (4), 401-403.—When *Salmonella hadar* is grown

under suitable conditions, its cell-free extract decarboxylates lysine selectively in the presence of other amino acids. The micro-organism (strain 1281) is incubated for 24 hr. at 25° under liquid paraffin in a medium containing trypticase soy broth (1%), NaCl (0.5%),  $Na_2HPO_4$  (0.25%),  $NaH_2PO_4$  (0.25%), Bovril (0.3%) and L-lysine hydrochloride (1%), and adjusted to a pH value between 6.2 and 6.5. After three passages, 100 ml of the medium is inoculated and incubated as previously, the cells are centrifuged, washed, suspended in 15 ml of water, held in a 9-kc Raytheon sonic oscillator for 60 min. and centrifuged to remove the cell debris. The protein for analysis (1 g) is hydrolysed with 6 N HCl (50 ml) at 120° to 125° for 35 hr. and the hydrolysate is evaporated three times *in vacuo*. The residue is dissolved in 0.1 M citrate buffer of pH 5. The lysine content is determined in a Warburg bath at 37° by using 2 ml of the hydrolysate soln. and 0.5 ml of the cell-free extract, and measuring the  $CO_2$  evolved. The method is applied to human serum albumin, casein, edestin, zein and human hair.

H. N. S.

**5370. Quantitative colorimetric determination of tryptophan.** J. Fischl (Chem. Lab., "Assaf Harofe" Government Hosp., Zrifin, Israel). *J. Biol. Chem.*, 1960, **235** (4), 999-1001.—*Procedure*—To the sample containing 5 to 50  $\mu$ g of tryptophan in aq. soln. (0.5 ml) add glacial acetic acid (2 ml), mix, add  $H_2SO_4$  (1 ml), mix, add 1 drop of satd.  $K_2S_2O_8$  soln. and 1 drop of 5% (v/v) thioglycolic acid in acetic acid, and mix again. After 10 to 15 min. measure the extinction at 530 to 550 m $\mu$ . The order of the addition of the reagents is important and must be strictly followed. Seventeen other amino acids and traces of phenol do not interfere. The results, obtained with protein hydrolysates, are reproducible and compare favourably with those given by other methods. The use of  $K_2S_2O_8$  as the oxidising agent is recommended except for the determination in proteins without previous hydrolysis; in this case 3%  $H_2O_2$  is used.

J. N. ASHLEY

**5371. Determination of tryptophan in natural media. II. The stability of tryptophan during alkaline hydrolysis carried out in the presence of carbohydrates.** A. Drèze (Lab. de Biochem., Fac. de Méd., Univ. Libre de Bruxelles, Belgium). *Bull. Soc. Chim. Biol.*, 1960, **42** (4), 407-417.—Pure DL-tryptophan was subjected to the conditions of alkaline hydrolysis that would be usual in liberating it from natural media, in the presence of carbohydrates [partially hydrolysed potato starch (prep. described), gum acacia or cellulose]. The recovery of tryptophan was determined by chromatography on a starch column, when, besides the tryptophan peak, a peak due to an unidentified substance reacting with ninhydrin and a yellow peak were obtained. Recovery was found to be much improved with lower concn. of carbohydrate, produced by diluting the soln. with alkali, but the carbohydrate in the diluted soln. acted as a protecting agent for the tryptophan. Stannous chloride and EDTA seem to be ineffective as protecting substances, but cysteine has a somewhat irregular protecting effect. The mechanism of the destruction of tryptophan is discussed. Barium hydroxide is preferable to NaOH, as the latter attacks glass vessels and the product of the reaction absorbs tryptophan. It is shown that L-tryptophan behaves in the same way as the racemate. Time of hydrolysis is shown to be important and the following conditions for good

recovery are recommended for 1 to 2 mg of tryptophan—1 g of treated starch, 30 ml of 5.5 N Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (25.2 g and 18 ml of H<sub>2</sub>O), and hydrolysis at 120° for 20 hr. in a sealed tube.

E. J. H. BIRCH

**5372. Polarographic determination of tyrosine, tryptophan and phenylalanine in the presence of each other.** D. Monnier, J. Vogel and P. E. Wenger (Geneva Univ., Switzerland). *Anal. Chim. Acta*, 1960, **22** (4), 369-383 (in French).—In a mixture of the three amino acids, the tryptophan (I) is first pptd. with mercuric acetate and the ppt. is separated by centrifugation. The tyrosine (II) in the soln. is nitrated by boiling with 0.15 N HNO<sub>3</sub> and a few crystals of NaNO<sub>2</sub>, and the nitration product is determined polarographically. Phenylalanine (III) is not nitrated by 0.15 N HNO<sub>3</sub>. The ppt. containing the I is boiled with 1.5 N HNO<sub>3</sub> and the nitrated I is determined polarographically. In a second sample the three amino acids are nitrated with 10 N HNO<sub>3</sub>, the nitrated I is separated by pptn. with mercuric acetate, the II is destroyed by oxidation with KMnO<sub>4</sub> in the presence of AgNO<sub>3</sub>, and the III is determined polarographically. The methods are applied to the determination of II in blood albumin and to the determination of all three acids in peptone. The 14 other amino acids present in peptone do not interfere.

H. N. S.

**5373. Determination of cystine by the sodium azide-iodine reaction.** Z. Kurzawa (Inst. Technol., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 325-326.—The consumption of iodine in the catalysis of the reaction  $2\text{NaN}_3 + \text{I}_2 \rightarrow 2\text{NaI} + 3\text{N}_2$  by cystine was used for its determination (0.05 to 1.0 mg) in insulin, hair, wool, flour and beer with an accuracy of  $\pm 1\%$ . The procedure is claimed to be simpler than all other known methods.

L. SMAKOWSKI

**5374. Determination of small amounts of cysteine alone and in the presence of cystine by means of the sodium azide-iodine reaction.** Z. Kurzawa and A. Suszka (Inst. Technol., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 327-329.—Reaction between  $\text{NaN}_3$  and iodine in aq. soln. is induced by both cysteine and cystine. The high rate of reaction in the presence of cysteine and the low one in the presence of cystine permitted a method for the determination of cysteine in the presence of cystine and *vice versa* to be developed. Cysteine (0.001 to 0.18 mg per 100 ml) and cystine (0.05 to 0.8 mg per 100 ml) were determined in aq. soln. (e.g., beer and milk) by measuring the consumption of iodine. The method is claimed to be accurate, rapid and simple.

L. SMAKOWSKI

**5375. Determination of methionine alone and in the presence of cystine by means of the sodium azide-iodine reaction.** Z. Kurzawa (Inst. Technol., Poznań, Poland). *Chem. Anal., Warsaw*, 1960, **5** (2), 331-332.—A method of determination of methionine (0.30 to 15 mg per 100 ml) is described. The high rate of the  $\text{NaN}_3$ -iodine reaction in the presence of methionine and the low one in the presence of cystine permits a method for the determination of methionine in the presence of cystine and *vice versa* to be developed. The method of determination of methionine was found to be much less sensitive than the corresponding one for cysteine and cystine (Kurzawa and Suszka, *Anal. Abstr.*, 1960, **7**, 5374).

L. SMAKOWSKI

**5376. Identification of kynurenine and xanthurenic acid in urine.** M. Kaláb (Gastroenterol. Lab., Med. Fac., Palacký Univ., Olomouc, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (4), 1220-1224 (in Russian).—A modification of the method of Dalglish (*Biochem. J.*, 1950, **52**, 3) is described. *Procedure*—To 5 ml of the urine in a centrifuge tube add a satd. soln. of Hg acetate in 25% acetic acid (2.5 ml). Centrifuge for 10 min., remove the supernatant liquid, mix the residue with H<sub>2</sub>O (5 ml) and centrifuge again. To the residue add H<sub>2</sub>O (1 ml) and into the suspension introduce H<sub>2</sub>S for about 5 min. Centrifuge and analyse the supernatant liquid chromatographically on Whatman No. 1 paper (20- $\mu$ l portions) with the use of the system methanol - *n*-butanol - benzene - H<sub>2</sub>O (2:1:1:1) and 20% KCl soln. as solvents. The separated spots were observed in u.v. light with the use of the following detecting reagents (i) for kynurenine—ninhydrin soln. (0.2%) in ethanol, *p*-dimethylaminobenzaldehyde soln. (0.5 g in 100 ml of ethanol with 1 ml of conc. HCl) and *p*-dimethylaminobenzaldehyde soln. (1% in acetone with 10% of conc. HCl); (ii) for xanthurenic acid—Pauli's reagent and FeCl<sub>3</sub> soln. (0.5%) in ethanol.

J. ŽYKA

**5377. Modification of the amino groups of the peptide component of subtilisin-modified ribonuclease. [Determination of acetyl content in acetylated peptide.]** P. J. Vithayathil and F. M. Richards (Dept. of Biochem., Yale Univ., New Haven, Conn., U.S.A.). *J. Biol. Chem.*, 1960, **235** (4), 1029-1037.—A specially constructed apparatus is used for the determination with 0.5  $\mu$ mole of the acetylated peptide which is mixed with 25% w/v toluene-*p*-sulphonic acid and heated at 100° for 3 hr. in the evacuated apparatus. The dil. acetic acid is collected in another part of the same apparatus and is titrated in the same apparatus with 0.0048 N NaOH to phenolphthalein. The recovery of acetic acid is 91 to 96%.

J. N. ASHLEY

**5378. Application of density-gradient electrophoresis to the separation of serum proteins.** K. S. Wiarda, A. J. Hyman and A. A. H. Kassenaar (Univ. Hosp., Leiden, The Netherlands). *Clin. Chim. Acta*, 1960, **5** (2), 289-295 (in English).—Results in different buffer soln. are compared, and resolution and mobilities of the protein fractions are described.

H. F. W. KIRKPATRICK

**5379. Paper electrophoresis of proteins in acid buffer.** J. H. Geller, J. H. Custer and C. A. Zittle (Eastern Regional Res. Lab., Philadelphia, Pa., U.S.A.). *J. Chromatography*, 1960, **3** (4), 369-371 (in English).—A buffer soln. consisting of lactic and propionic acids adjusted to pH 2.3 to 2.6 with NaOH permits the paper electrophoresis of the  $\alpha$ -casein complex and its components. Sharp bands are produced which are characteristic of Ca-sensitive and Ca-insensitive  $\alpha$ -caseins. Electrophoresis is carried out at 25° at 250 V for 5 hr. G. P. Cook

**5380. Elimination of background staining in the periodic acid-Schiff method for protein-bound carbohydrates in paper electrophoresis.** M. N. Green, E. Rieckstniec, O. Valdes-Diaz and H. Shwachman (Children's Cancer Res. Foundation, Boston, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1960, **55** (1), 158-163.—The formation of variable background colours that interfere with the photometric scanning of stained paper strips is prevented by the exclusion of alcohol from the reagents and the standardisation



of their preparation, and by using minimum times for HIO<sub>4</sub> oxidation and fuchsin-sulphite treatment. With the modified method, the depth of colour is proportional to the amount of serum. The error ranges from 1.4 to 5.1%, according to the serum fraction.

W. H. C. SHAW

**5381. Effect of carboxymethylcellulose on the electrophoresis of serum proteins on paper.** R. Holmes and S. W. Wolfe (A. I. du Pont Inst., Wilmington, Del., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (1), 13-18.—A study is made of the electro-osmotic effects of carboxymethylcellulose (up to 2%) added to the barbitone buffer employed in paper electrophoresis. The substances studied include amino acids, sugars, surface-active agents and serum proteins, and the modifications in the patterns obtained are discussed. The separation of the components of  $\alpha$ -lipoproteins in calf serum and their separation from other constituents is described, and the value of carboxymethylcellulose in certain separations is considered.

W. H. C. SHAW

**5382. New staining procedure and method for the determination of serum lipoproteins separated by paper electrophoresis.** R. Straus and M. Wurm (St. Joseph Hosp., Burbank, Calif.). *Amer. J. Clin. Path.*, 1958, **29** (6), 581-589.—Serum is separated by paper electrophoresis in barbitone buffer (pH 8.6). Lipids are stained with Fat Red 7B (C.I. Solvent Red 19), and treatment of the electropherogram with NaClO results in a clear background and makes possible the easy recognition of 5 lipoprotein fractions. The relative concn. of these fractions is estimated by direct densitometry at 525 m $\mu$ .

P. NICHOLLS

**5383. Chromogenic groupings in the Lowry protein determination.** S.-C. Chou and A. Goldstein (Dept. of Pharmacol., Stanford Univ. Sch. of Med., Calif., U.S.A.). *Biochem. J.*, 1960, **75** (1), 109-115.—In the Lowry method (*Brit. Abstr. C.*, 1952, 160) the phenol reagent is reduced to give a blue colour; the colour yield of a completely hydrolysed protein is due to its content of tyrosine, tryptophan and cysteine, which are the only amino acids that react significantly. Preliminary treatment with an alkaline copper soln. greatly increases the colour given by proteins. This is due mainly to sequences of amino acids containing functional side-chains. Dipeptides that contain a histidine, arginine or glutamic acid residue are particularly chromogenic.

J. N. ASHLEY

**5384. Determination of cuprous ion in copper proteins.** G. Felsenfeld (Pittsburgh Univ., Pa., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (2), 247-251.—Incorrect results for Cu<sup>+</sup> in certain proteins by the method of Klotz (*Science*, 1955, **121**, 477), with 2:2'-diquinoyl in glacial acetic acid, are attributed to the reduction of Cu<sup>+</sup> by mercapto groups present in the protein. The effect can be eliminated by the addition of sodium *p*-mercuribenzoate in the proportion of at least 3 moles per mole of Cu. Reduction of Cu<sup>+</sup> may also be avoided by the addition of EDTA, with which slightly different results are obtained. These and the mechanism of the reactions are discussed.

W. H. C. SHAW

**5385. Determination of neuraminic acid in human red blood corpuscles.** G. Manfredi (Ist. Clin. Pediatr., Univ., Bologna, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1960, **36** (10), 447-449.—Determinations of erythrocytic neuraminic acid content of blood

from 15 normal babies are reported. The neuraminic acid in the haemoglobin-free material was determined by reaction with Bial's reagent according to the method of Böhm (*cf. Anal. Abstr.*, 1954, **1**, 2755). Results obtained varied only from 15.5 to 22.8 mg per 100 ml, with a mean of 19.2 mg per 100 ml.

E. C. APLING

**5386. Sterol analysis by gas chromatography.** R. K. Beerthuis and J. H. Recourt (Unilever Res. Lab., Vlaardingen, Netherlands). *Nature*, 1960, **186**, 372-374.—Sterols differing in the total number of carbon atoms can be separated and determined by chromatography at 287° on a column (90 cm  $\times$  4 mm) packed with 20% w/w of silicone oil on 150 to 178- $\mu$  Celite, with a nitrogen flow-rate of 24 ml per min. The silicone oil used is the residue from a molecular distillation at 200° and 2  $\mu$  pressure and the Celite is pre-treated with acid and dichlorodimethylsilane to render it as inert as possible. Before use the column is conditioned for 2 days at the working temp. Under these conditions the i.r. spectra of cholesterol showed that no structural changes occurred on passage through the column. Retention volumes relative to cholesterol are tabulated.

K. A. PROCTOR

**5387. Comparison of results from three methods for the determination of serum cholesterol.** D. Bargeton, M. E. Tricaud-Redel and P. Gros (Soc. Théraplix, Paris). *Rev. Franç. Étud. Clin. et Biol.*, 1959, **4**, 326-334.—Three methods for the determination of serum cholesterol, viz. the Schoenheimer-Sperry, the Grigaut and the Delsal methods, were evaluated. The first method showed the smallest standard error in replicate analyses. The Grigaut and the Delsal methods, when compared with the Sperry method (*J. Biol. Chem.*, 1943, **150**, 315), had large inherent errors. Data on Abell's method taken from the literature indicated that it had the same precision as the Sperry method.

CHEM. ABSTR.

**5388. Observations on Brown's method for the determination of urinary oestrogens.** G. Cavina, E. Anselmi, A. Menotti and A. Natoli (Biol. Lab., Ist. Sup. Sanit., Roma). *R.C. Ist. Sup. Sanit.*, 1960, **23** (3-4), 269-284.—Oestriol (I), oestrone (II) and oestradiol (III) are determined by modifications of Brown's method (*Biochem. J.*, 1955, **60**, 185; *J. Endocrin.*, 1957, **16**, 41, 49). Six stages are involved. (i) Hydrolyse the urine with HCl and extract with ether. (ii) Wash the ether extract with various controlled alkaline mixtures and evaporate to dryness. (iii) Separate I in the dry residue from II and III by extraction from a benzene-hexane soln. with H<sub>2</sub>O. The aq. layer (A) contains I, the benzene-hexane layer (B) II and III. (iv) Saponify A with NaOH, extract with ether, and extract the ether with dil. NaOH soln. Pool the alkaline fractions, methylate with boric acid and dimethyl sulphate, oxidise impurities with NaOH and H<sub>2</sub>O<sub>2</sub>, extract with benzene, wash with water and separate the methyl ether of I by chromatography on an alumina column. (v) Extract B with dil. NaOH soln., saponify the extract with more NaOH, extract with benzene, add *n*-hexane and extract the mixture with dil. NaOH. Methylate and oxidise as for A and extract with *n*-hexane, wash with H<sub>2</sub>O and separate the methyl ethers of II and III by chromatography on an alumina column, with 25% benzene in hexane to elute pigments followed by 40% benzene in hexane to elute

the methyl ether of **II** and by 80% benzene in hexane to elute the methyl ether of **III**. (vi) Evaporate the chromatograph fractions containing **I**, **II** and **III** to dryness with 2% quinol soln. in ethanol and complete the determination as in Brown's method. Mean recoveries are 74, 89 and 75% for **I**, **II** and **III**, respectively, the losses having been shown to occur in the first extraction and washing stages.

J. I. M. JONES

**5389. Identification and determination of corticoid-like steroids of pharmaceutical interest by paper chromatography.** G. Cavina and E. Cingolani (Biol. Lab., Ist. Sup. Sanit., Roma). *R. C. Ist. Sup. Sanit.*, 1960, **23** (3-4), 254-268; *Farmaco, Ed. Prat.*, 1960, **15** (4), 246-258.—The chromatographic separation and determination in biological fluids and pharmaceutical preparations of steroids, in particular prednisone, prednisolone, cortisone, hydrocortisone, triamcinolone and dexamethasone, are described. Chromatography is carried out with either  $\text{CHCl}_3$ -formamide, propanediol-toluene, toluene-heptane-methanol-water, or toluene-ethyl acetate-methanol-water. Pharmaceutical products are extracted with  $\text{CHCl}_3$ . Tables of the relative separations of above-mentioned steroids on the chromatogram with the various solvent mixtures are given. The chromatogram spots are revealed by u.v. light, blue tetrazolium, 2N NaOH or isoniazid. Quant. determinations may be made by cutting out spots, extracting and measuring the extinction in methanol between 200 and 260  $\mu$ , in  $\text{H}_2\text{SO}_4$  between 220 and 700  $\mu$  or by treatment with blue tetrazolium. Tables of spectrographic data are given. Recoveries are from 90 to 92%.

J. I. M. JONES

**5390. Rapid spectrophotometric assay of monoamine oxidase based on the rate of disappearance of kynuramine.** H. Weissbach, T. E. Smith, J. W. Daly, B. Witkop and S. Udenfriend (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1960, **235** (4), 1160-1163.—The oxidase readily oxidatively deaminates kynuramine (the decarboxylation product of kynurenine) to the corresponding aldehyde, which then condenses intramolecularly to 4-hydroxyquinoline. The determination depends on measurement of the disappearance of the amine at 360  $\mu$  by means of the change in extinction at this wavelength, which is followed spectrophotometrically.

J. N. ASHLEY

**5391. Manometric assay and properties of pancreatic cholesterol esterase.** M. Korzenovsky, E. R. Diller, A. C. Marshall and B. M. Auda (Biochem. Res. Div., Lilly Res. Lab., Indianapolis, Ind., U.S.A.). *Biochem. J.*, 1960, **76** (2), 238-245.—The hydrolysis and synthesis of cholesteryl oleate by the esterase is followed manometrically in a  $\text{NaHCO}_3$ - $\text{CO}_2$  buffer system. The assay is based on the fact that, for each mole of ester which is synthesised or hydrolysed, an equiv. of  $\text{CO}_2$  is absorbed into or released from the aq. phase. The optimum composition of the colloidal substrate and conditions for synthesis and hydrolysis of the ester are given. The results agree fairly well with those obtained by the colorimetric method of Sperry and Webb (*J. Biol. Chem.*, 1950, **187**, 97).

J. N. ASHLEY

**5392. Titrimetric method for the measurement of the cholinesterase activity of blood serum and its application to the determination of several compounds possessing anticholinesterase activity.** R. M. Fournier. *Mém. Poudres*, 1958, **40**, 403-412 (in

French).—The method is a modification of that due to Vincent *et al.* (*Ann. Biol. Clin.*, 1944, **2**, 35). The amount of organic acid released from acetylcholine by cholinesterase is reduced in the presence of compounds with anticholinesterase activity, e.g., methyl sarin (**I**), ethyl sarin (**II**), tabun (ethyl dimethylphosphoramidocyanide) (**III**) and tetraethyl pyrophosphate (**IV**). The reduction in the amount of acidity liberated is measured by titration. *Procedure*.—Into a test-tube place phosphate buffer soln. (pH 7.5) (25 ml), diluted horse serum (1 ml) and phenol red soln. [0.02% in aq. ethanol (1:1)] (10 drops). Into a second tube place 0.2% acetylcholine hydrochloride soln. (10 ml), water (10 ml) and phenol red soln. (10 drops). Place both tubes in a thermostat at  $38^\circ \pm 0.1^\circ$  for 10 min. and then neutralise the second tube to the colour of the blank with 0.01 N NaOH. Add diluted horse serum (1 ml) and the sample soln. (up to 10 ml). Replace the tubes in the thermostat and repeat the titration at intervals of exactly 5 min. for 40 min. The concn. of the inhibitor in the sample can then be read off from standard curves prepared with known amounts of the pure compounds. The method is suitable for the determination of up to 1  $\mu$ g of **I**, 0.5  $\mu$ g of **II**, 1  $\mu$ g of **III** and 0.1  $\mu$ g of **IV**.

W. T. CARTER

**5393. Titrimetric method for the determination of creatine phosphokinase.** A. K. Cho, W. L. Haslett and D. J. Jenden (Dept. of Pharmacol. UCLA Med. Centre, Univ. of California, Los Angeles 24, U.S.A.). *Biochem. J.*, 1960, **75** (1), 115-119.—The method described depends on the fact that a  $\text{H}^+$  is quant. liberated at pH 9.0 in the reaction between adenosine triphosphate and creatine, in the presence of the phosphokinase, to give adenosine diphosphate and creatine phosphate. A const. pH titration can therefore be carried out, and the rate of addition of the base is equal to the rate of the reaction involving the enzyme. The method is simple and extremely sensitive, and a determination takes  $\approx 10$  min. It does not use other enzyme systems and is suitable for inhibitor studies. Under the specified conditions it is specific for creatine phosphokinase. Very dilute soln. of the enzyme are assayed with great accuracy. In the absence of substrates other than adenosine triphosphate and creatine, a significant shift in pH is produced only by hydrolysis of adenosine triphosphate or transphosphorylation of creatine; the former is allowed for by a control carried out in the absence of creatine and is very small in practice.

J. N. ASHLEY

**5394. The lactic dehydrogenase of *Propionibacterium pentosaceum*.** [Assay methods.] R. Molinari and F. J. S. Lara (Dept. of Biochem., Fac. of Med. of Ribeirão Preto, Univ. of São Paulo, Brazil). *Biochem. J.*, 1960, **75** (1), 57-65.—Several methods are described for the assay of the enzyme from the bacterium which oxidises lactate to pyruvate in the presence of suitable H acceptors. In the indophenol method, 2,6-dichlorophenolindophenol is used as the H acceptor; extinctions are determined spectrophotometrically at 600  $\mu$  and conditions are chosen so that the rate of reduction of the dye is proportional to the amount of enzyme used. In the quinone method, the same conditions apply, but 1:2-naphthaquinone-4-sulphonate is used as the H acceptor, and extinctions are measured at 305  $\mu$ . The methylene blue and phenazine methosulphate assays are manometric methods, and the conditions are chosen so that consumption of O is proportional to the amount of enzyme.

J. N. ASHLEY

5395. **Measurement of transaminases in serum.** H. Yatzidis (Hippocratean Univ. Hosp., Univ. of Athens Sch. of Med., Greece). *Nature*, 1960, **186**, 79-80.—Details of a colorimetric method are given for the determination of glutamic-oxalacetic and glutamic-pyruvic transaminases. The serum is incubated at 37° for 1 hr. with the appropriate substrate (prep. described), and the reaction is stopped by addition of aniline citrate. 2:4-Dinitrophenylhydrazine soln. is added, followed, after 5 min., by NaOH. The extinction is read at 500 m $\mu$  after 30 min. By the use of this method interference by  $\alpha$ -oxoglutaric acids is avoided.

H. F. W. KIRKPATRICK

5396. **Mutarotase from *Penicillium notatum*. I. Purification, assay, and general properties of the enzyme.** R. Bentley and D. S. Bhate (Grad. Sch. of Publ. Hlth., Univ. of Pittsburgh, Pa., U.S.A.). *J. Biol. Chem.*, 1960, **235** (5), 1219-1224.—The enzyme is determined by direct measurement of the net amount of  $\beta$ -glucose formed from  $\alpha$ -glucose in a given time. The method is based on the more rapid oxidation of  $\beta$ -glucose than of  $\alpha$ -glucose by Br in phosphate buffer (pH 5.7) at 0°. Excess of Br is removed by extraction with chloroform-maize oil (1:1), and the unoxidised glucose is determined by the Nelson-Somogyi method. Other methods of determination are discussed.

J. N. ASHLEY

5397. **Determination of riboflavine and its coenzymes in tissues.** P. Cerletti and P. Ipata (Inst. of Biol. Chem., Univ. of Rome, Italy). *Biochem. J.*, 1960, **75** (1), 119-124.—An easy and rapid method for the separation and determination is described. The tissue is extracted with phosphate buffer and the riboflavine and its coenzymes are separated on Amberlite IRC-50 (H<sup>+</sup> form). Each is determined fluorimetrically by a standard method.

J. N. ASHLEY

See also Abstracts—5148, <sup>137</sup>Cs in biological material. 5263, N in protein hydrolysates. 5276, Determination of 3-deoxy sugars. 5277, Determination of mucopolysaccharides. 5287, Dimethylnitrosamine in urine. 5409, Identification of adrenaline and noradrenaline. 5418, Nitrofurantoin in urine. 5485, Apparatus for respired air. 5490, Chromatography of amino acids. 5507, Spectrofluorimeter for biochemical analysis.

#### Pharmaceutical analysis

5398. **Contribution to the microscopic characterisation and identification of drugs. II.** M. Brandstätter-Kuhnert, A. Kofler and O. Kostenzer (Pharmakogn. Inst., Univ., Innsbruck, Austria). *Sci. Pharm.*, 1960, **28** (1), 7-15.—Melting-points, crystal forms, eutectic temperatures and other characteristics of 33 drugs are tabulated. (Cf. Brandstätter-Kuhnert and Kofler, *Anal. Abstr.*, 1960, **7**, 1535.)

A. R. ROGERS

5399. **Photometric titrations in non-aqueous media. I. Determination of weak bases, with methyl violet as indicator.** H. Ellert, T. Jasiński and K. Marcinkowska (Dept Pharm. Chem., Med. Acad., Gdansk). *Acta Polon. Pharm.*, 1960, **17** (1), 29-39.—The investigations were carried out on weak bases in a mixture of glacial acetic acid and acetic anhydride, with 0.1 N HClO<sub>4</sub> in glacial acetic acid as titrant and methyl violet as indicator. The colour change was measured photometrically. Statistics

and curves are given relating the light absorption  $A$  to the vol.  $V$  of HClO<sub>4</sub> for the following weak organic bases and their salts—benzocaine, adrenaline, phenazone, caffeine, 1- and 2-naphthylamine, narceine, hexamine, sulphanilamide, sulphathiazole, sulphamethazine, sulphapyridine, sulphaguanidine, quinine sulphate and hydrochloride, and amethocaine.

W. B. MIASKOWSKI

5400. **Reactions between alkaloids and tetraphenylboron and their analytical application. A heterometric study.** M. Bobtelsky and M. M. Cohen (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1960, **22** (4), 328-338.—Thirteen heterocyclic compounds of N, including several alkaloids, are titrated with 0.001 to 0.005 M Na tetraphenylboron by the heterometric method (cf. *Anal. Abstr.*, 1956, **3**, 12). The titration curves provide an indication of the constitution of the intermediate and final compounds formed.

H. N. S.

5401. **New data on the characterisation and determination by paper chromatography of alkaloids derived from piperidine.** J. Massicot (Mus. National d'Hist. Nat., 63 rue Buffon, Paris, France). *Bull. Soc. Chim. France*, 1959, (11-12), 1825-1828.—Piperidine alkaloids, especially those from the poppy, are best separated on Whatman No. 1 paper buffered to pH 9 (borax buffer) with a solvent of ethyl ether-dioxan-acetic acid-water (13:7:2:2) by the ascending technique at 20°. A much greater sensitivity in the revealing of the spots than is given by the usual Dragendorff reagent is obtained by spraying first with aq. KI soln. (0.16%) and then, after drying, with bismuth subnitrate soln. (0.1% in 0.5% aq. HClO<sub>4</sub>). The coloration obtained is the same as that with the usual reagent, but there is a yellow ring round the spots. A method is given for the extraction of alkaloids in small quantities from natural media. *Procedure*—About 100 mg (dry wt.) of material is ground with 10 ml of ethanol and, after filtering and washing, the ethanol soln. is evaporated and taken up in 1 ml of 2% aq. HCl and 2 ml of ethyl acetate, then decanted, and the vessel is rinsed with half that quantity of the same reagents. The org. layer is separated and the HCl soln. is extracted several times with 1 ml of ethyl acetate until the extract is no longer coloured. The aq. soln. is then made alkaline and extracted with ethyl acetate (3  $\times$  2 ml). The extract is evaporated, taken up in 0.1 ml of methanol and the soln. is used for chromatography. Investigation of the extraction procedure shows that the codeine spot is longer after extraction and this is considered to be due to overlapping of the spot by an oxidation product. Narcotine gives three spots, two of which are probably scission products (probably hydrocotarnine and opianic acid). The length of the spots is not proportional to the alkaloid content, but methods for using the spots quantitatively are discussed.

E. J. H. BIRCH

5402. **The polarographic determination of papaverine.** L. Faith (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Farmácia*, 1960, **29** (3), 79-81.—By treatment with conc. HNO<sub>3</sub> papaverine is converted into the polarographically active nitro derivative, which yields a double wave; the height of the first wave can be used for analytical determinations. The method was used for the determination of papaverine in tablets with an error of up to  $\pm 3\%$ . *Procedure*—Dissolve the finely powdered sample in H<sub>2</sub>O, dilute

to 25 ml, and evaporate 0.5 to 1 ml of the clear supernatant liquid on a water bath. Add  $\text{HNO}_3$  (65%) (1 ml) and heat for 30 min. at  $60^\circ$  to  $70^\circ$ . Cool, add KOH soln. (20%) (10 ml) and gelatin soln. (0.5%) (0.1 ml), and set aside for 15 min.; remove O with a stream of N and register the polarographic wave from  $-0.4$  V. Compare with a calibration curve.

J. ŽYKA

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CHEM. ABSTR.

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A. R. ROGERS

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H. F. W. KIRKPATRICK

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technique, and their significance in the identification and differentiation of these compounds is discussed.

A. R. ROGERS

**5411. Spectrophotometric assay for combinations of ethinyloestradiol and methyltestosterone.** S. Klein, A. E. James and M. M. Tuckerman (Temple Univ., School of Pharmacy, Philadelphia, Pa.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (5), 314-316. —The u.v. absorption spectrum of ethinyloestradiol (I) shows a max. at 298 m $\mu$  in 0.3 N methanolic KOH, with  $E_{1\text{cm}}^{1\%} = 90$ ; in 0.01 N methanolic HCl the max. is at 281 m $\mu$  and the value of  $E_{1\text{cm}}^{1\%}$  at 241 m $\mu$  is 18.0. The absorption spectrum of methyltestosterone (II) in methanol is independent of pH; max. absorption is at 241 m $\mu$  with  $E_{1\text{cm}}^{1\%} = 508$  and the value at 298 m $\mu$  is 3.25. Simultaneous determination of both I and II in ratios from 6:1 to 1:4 is possible by measurement of the extinctions at 241 m $\mu$  in acid and at 298 m $\mu$  in alkaline soln. The average error is  $\approx 2\%$ . Mixtures containing I and II in ratios from 1:200 to 1:500 are assayed for II by direct measurement of the extinction at 241 m $\mu$  in acid methanol. The method has been used for the assay of tablets and liquid preparations.

A. R. ROGERS

**5412. Assay and control of antibiotic discs.** A. Kirshbaum, J. Kramer and B. Arret (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (4), 249-258. —Methods are described for the assay of diagnostic discs prepared from any of the 21 antibiotics studied. The preparation of eight culture media, of suspensions of the test organisms selected and of control discs is given and results are discussed in relation to those obtained by an extraction method. All the methods given have 95% confidence limits of 67 to 150% of the assay value.

W. H. C. SHAW

**5413. PA 155A: a new antibiotic.** K. V. Rao (John L. Smith Memorial for Cancer Res., Maywood, N.J., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (5), 312-315. —A description is given of the chemical and physical properties of PA 155A, one of a group of antibiotics produced by *Streptomyces albus*. These include optical rotation, u.v. and i.r. spectra, colour reactions, picrate formation and a column-chromatographic procedure for purification of the substance.

W. H. C. SHAW

**5414. Microchemical identification of some modern analgesics.** E. G. C. Clarke (Royal Vet. Coll., London). *Bull. Narcotics, U.N. Dept. Social Affairs*, 1959, **11** (1), 16-29. —Crystal and colour tests are given for 51 analgesic drugs, with 24 photographs of crystal form.

CHEM. ABSTR.

**5415. Spectrophotometric determination of diprophylline and phenobarbitone in their mixtures.** H. Bukowska and J. Gierlowska (Inst. of Pharmacy, Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 309-315. —An u.v. spectrophotometric method for the determination of diprophylline and phenobarbitone in their mixtures and in tablets is described. The extinction of the mixture is measured at 240 m $\mu$  and 272 m $\mu$ , and the composition is calculated from the formulae given. The samples contained 100 to 150 mg of diprophylline and 10 to 100 mg of phenobarbitone, giving ratios from 1:1 to 10:1. A buffer soln. (pH 9.5) was used to obtain a sample soln. containing  $\approx 10 \mu\text{g}$  of diprophylline per ml. The method permits the determination of both constituents in a single soln. prepared

directly from tablets. The maximum error of the diprophylline determination was 0.4%, and of the phenobarbitone determination 3.0%.

L. SMAKOWSKI

**5416. Spectrophotometric determination of amphetamine [in illicit drugs].** C. Milos (Alcohol & Tobacco Tax Lab., Internal Revenue Service, New York, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 229-233. —The sample is dissolved in 0.1 N H<sub>2</sub>SO<sub>4</sub> and the amounts of quinine and diamorphine, if present, are calculated from measurements of extinction at 280 and 348 m $\mu$ . An aliquot is then made alkaline to phenolphthalein with Na<sub>2</sub>PO<sub>4</sub> and distilled. The extinction of the distillate, acidified with H<sub>2</sub>SO<sub>4</sub>, is measured at 257 m $\mu$ , the result giving the amount of amphetamine present. If the sample contains much lactose the amphetamine is first extracted from an alkaline solution with CHCl<sub>3</sub>.

A. A. ELDRIDGE

**5417. Determination of meprobamate as the dioxanthyl derivative.** E. B. Dechene (Res. and Control Lab., Charles E. Frost & Co., Montreal, Quebec, Canada). *J. Pharm. Pharmacol.*, 1960, **12** (4), 255-256. —*Procedure*—The sample (0.1 g) is treated with 9-xanthanol (0.3 g) in glacial acetic acid (5 ml), seeded with 5 to 10  $\mu\text{g}$  of cryst. dioxanthyl meprobamate and set aside for 16 hr.; 80% aq. isopropyl alcohol (45 ml) is added and the mixture is refrigerated for 1 hr. The crystals are transferred to a sintered glass filter with 15 ml of aq. isopropyl alcohol, and dried to const. wt. at 100°; wt. of crystals  $\times 0.3769 = \text{wt. of meprobamate}$ . A solubility correction of 0.004 g is applied. The corrected recovery is  $\approx 96\%$ . Solubilities in 13 solvents are tabulated. The N content and m.p. of the derivative recrystallised from methanol were 4.80% and 188° to 189°, respectively.

A. R. ROGERS

**5418. Polarographic determination of 5-nitrofurantoin derivatives. II. Determination of 1-(5-nitro-furfurylideneamino)hydantoin (nitrofurantoin) in drugs and urine.** H. Marciszewski (Inst. Pharm., Warsaw). *Acta Polon. Pharm.*, 1960, **17** (1), 23-28. —The method is based on the fact that nitrofurantoin (I) is reduced on the dropping mercury electrode producing two inflections, one corresponding to the reduction of the N-group which is easily measurable and sufficiently accurate for quant. use (error  $\approx 2\%$  for substances containing 4%), and the second wave probably relates to  $-\text{CH}_2\text{N}$ -groups. The pH has no influence on the results within the range 1.9 to 6.7. The application of the polarographic method was also studied in respect of rapid determinations of I in urine without preliminary separation.

W. B. MIAKOWSKI

**5419. Analytical characteristics of some long-acting sulphonamides.** G. Bellomonte, A. Calò and C. Cardini (Lab. de Chim., Ist. Sup. Sanità, Rome). *Pharm. Acta Helv.*, 1960, **35** (4-5), 141-147 (in French). —Curves of u.v. absorption are given for soln. of 6-methoxy-3-sulphanilamidopyridazine, 6-chloro-3-sulphanilamidopyridazine, 2-phenyl-3-sulphanilamidopyridazine and 2:4-dimethoxy-6-sulphanilamidopyrimidine in ethanol, 0.1 N NaOH and 2 N HCl, and i.r. spectra from 5000 to 650 cm<sup>-1</sup> for liquid paraffin mulls. The four compounds can be partially separated by paper chromatography with *n*-butanol-aq. NH<sub>3</sub>-H<sub>2</sub>O (4:1:5) as mobile phase or by electrophoresis in 0.012 N NaOH at a potential gradient of  $\approx 17 \text{ V per cm}$ .

A. R. ROGERS

to 25 ml, and evaporate 0.5 to 1 ml of the clear supernatant liquid on a water bath. Add  $\text{HNO}_3$  (65%) (1 ml) and heat for 30 min. at 60° to 70°. Cool, add KOH soln. (20%) (10 ml) and gelatin soln. (0.5%) (0.1 ml), and set aside for 15 min.; remove O with a stream of N and register the polarographic wave from -0.4 V. Compare with a calibration curve. J. ŽYKA

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technique, and their significance in the identification and differentiation of these compounds are discussed.

A. R. ROGERS

**5411. Spectrophotometric assay for combinations of ethinylestradiol and methyltestosterone.** S. Klein, A. E. James and M. M. Tuckerman (Temple Univ., School of Pharmacy, Philadelphia, Pa.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (5), 314-316.—The u.v. absorption spectrum of ethinylestradiol (I) shows a max. at 298 m $\mu$  in 0.3 N methanolic KOH, with  $E_{1\text{cm}}^{1\%} = 90$ ; in 0.01 N methanolic HCl the max. is at 281 m $\mu$  and the value of  $E_{1\text{cm}}^{1\%}$  at 241 m $\mu$  is 18.0. The absorption spectrum of methyltestosterone (II) in methanol is independent of pH; max. absorption is at 241 m $\mu$  with  $E_{1\text{cm}}^{1\%} = 508$  and the value at 298 m $\mu$  is 3.25. Simultaneous determination of both I and II in ratios from 6:1 to 1:4 is possible by measurement of the extinctions at 241 m $\mu$  in acid and at 298 m $\mu$  in alkaline soln. The average error is  $\approx 2\%$ . Mixtures containing I and II in ratios from 1:200 to 1:500 are assayed for II by direct measurement of the extinction at 241 m $\mu$  in acidic methanol. The method has been used for the assay of tablets and liquid preparations.

A. R. ROGERS

**5412. Assay and control of antibiotic discs.** A. Kirshbaum, J. Kramer and B. Arret (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (4), 249-258.—Methods are described for the assay of diagnostic discs prepared from any of the 21 antibiotics studied. The preparation of eight culture media, of suspensions of the test organisms selected and of control discs is given and results are discussed in relation to those obtained by an extraction method. All the methods given have 95% confidence limits of 67 to 150% of the assay value.

W. H. C. SHAW

**5413. PA 155A: a new antibiotic.** K. V. Rao (John L. Smith Memorial for Cancer Res., Maywood, N.J., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (5), 312-316.—A description is given of the chemical and physical properties of PA 155A, one of a group of antibiotics produced by *Streptomyces albus*. These include optical rotation, u.v. and i.r. spectra, colour reactions, picrate formation and a column-chromatographic procedure for purification of the substance.

W. H. C. SHAW

**5414. Microchemical identification of some modern analgesics.** E. G. C. Clarke (Royal Vet. Coll., London). *Bull. Narcotics, U.N. Dept. Social Affairs*, 1959, **11** (1), 16-29.—Crystal and colour tests are given for 51 analgesic drugs, with 24 photographs of crystal form.

CHEM. ABSTR.

**5415. Spectrophotometric determination of diprophylline and phenobarbitone in their mixtures.** H. Bukowska and J. Gierlowska (Inst. of Pharmacy, Warsaw). *Chem. Anal., Warsaw*, 1960, **5** (2), 309-315.—An u.v. spectrophotometric method for the determination of diprophylline and phenobarbitone in their mixtures and in tablets is described. The extinction of the mixture is measured at 240 m $\mu$  and 272 m $\mu$ , and the composition is calculated from the formulae given. The samples contained 100 to 150 mg of diprophylline and 10 to 100 mg of phenobarbitone, giving ratios from 1:1 to 10:1. A buffer soln. (pH 9.5) was used to obtain a sample soln. containing  $\approx 10 \mu\text{g}$  of diprophylline per ml. The method permits the determination of both constituents in a single soln. prepared

directly from tablets. The maximum error of the diprophylline determination was 0.4%, and of the phenobarbitone determination 3.0%.

L. SMAKOWSKI

**5416. Spectrophotometric determination of amphetamine (in illicit drugs).** C. Milos (Alcohol & Tobacco Tax Lab., Internal Revenue Service, New York, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 229-233.—The sample is dissolved in 0.1 N H<sub>2</sub>SO<sub>4</sub> and the amounts of quinine and diamorphine, if present, are calculated from measurements of extinction at 280 and 348 m $\mu$ . An aliquot is then made alkaline to phenolphthalein with Na<sub>2</sub>PO<sub>4</sub> and distilled. The extinction of the distillate, acidified with H<sub>2</sub>SO<sub>4</sub>, is measured at 257 m $\mu$ , the result giving the amount of amphetamine present. If the sample contains much lactose the amphetamine is first extracted from an alkaline solution with CHCl<sub>3</sub>.

A. A. ELDRIDGE

**5417. Determination of meprobamate as the dioxanthyl derivative.** E. B. Dechene (Res. and Control Lab., Charles E. Frost & Co., Montreal, Quebec, Canada). *J. Pharm. Pharmacol.*, 1960, **12** (4), 255-256.—*Procedure*—The sample (0.1 g) is treated with 9-xanthanol (0.3 g) in glacial acetic acid (5 ml), seeded with 5 to 10  $\mu\text{g}$  of cryst. dioxanthyl meprobamate and set aside for 16 hr.; 80% aq. isopropyl alcohol (45 ml) is added and the mixture is refrigerated for 1 hr. The crystals are transferred to a sintered glass filter with 15 ml of aq. isopropyl alcohol, and dried to const. wt. at 100°; wt. of crystals  $\times 0.3769 = \text{wt. of meprobamate}$ . A solubility correction of 0.004 g is applied. The corrected recovery is  $\approx 96\%$ . Solubilities in 13 solvents are tabulated. The N content and m.p. of the derivative recrystallised from methanol were 4.80% and 188° to 189°, respectively.

A. R. ROGERS

**5418. Polarographic determination of 5-nitrofurantoin derivatives. II. Determination of 1-(5-nitro-furfurylideneamino)hydantoin (nitrofurantoin) in drugs and urine.** H. Marciszewski (Inst. Pharm., Warsaw). *Acta Polon. Pharm.*, 1960, **17** (1), 23-28.—The method is based on the fact that nitrofurantoin (I) is reduced on the dropping mercury electrode producing two inflections, one corresponding to the reduction of the N-group which is easily measurable and sufficiently accurate for quant. use (error  $\approx 2\%$  for substances containing 4%), and the second wave probably relates to  $-\text{CH}_2\text{N}$ -groups. The pH has no influence on the results within the range 1.9 to 6.7. The application of the polarographic method was also studied in respect of rapid determinations of I in urine without preliminary separation.

W. B. MIAKOWSKI

**5419. Analytical characteristics of some long-acting sulphonamides.** G. Bellomonte, A. Calò and C. Cardini (Lab. de Chim., Ist. Sup. Sanità, Rome). *Pharm. Acta Helv.*, 1960, **35** (4-5), 141-147 (in French).—Curves of u.v. absorption are given for soln. of 6-methoxy-3-sulphanilamidopyridazine, 6-chloro-3-sulphanilamidopyridazine, 2-phenyl-3-sulphanilamidopyridazine and 2:4-dimethoxy-6-sulphanilamidopyrimidine in ethanol, 0.1 N NaOH and 2 N HCl, and i.r. spectra from 5000 to 650 cm<sup>-1</sup> for liquid paraffin mulls. The four compounds can be partially separated by paper chromatography with *n*-butanol-aq. NH<sub>3</sub>-H<sub>2</sub>O (4:1:5) as mobile phase or by electrophoresis in 0.012 N NaOH at a potential gradient of  $\approx 17 \text{ V per cm}$ .

A. R. ROGERS

**5420. Colorimetric determination of sulphonamides in the presence of procaine penicillin.** G. Machek (Kontroll-Lab. der Biochemie, G.m.b.H., Kundl/Tirol, Austria). *Sci. Pharm.*, 1960, **28** (1), 1-7.—Determine the penicillin microbiologically and calculate the amount of procaine in the sample. Determine sulphonamide and procaine by diazotisation and coupling with N-(1-naphthyl)ethylenediamine and apply a correction for the contribution of the procaine to the total colour at 540 m $\mu$ . The method has been successfully applied to pharmaceutical powders and ointments. A. R. ROGERS

**5421. Identification of sulphamerazine in the presence of other sulphonamides.** A. Goudswaard (Rijksinst. Pharmacotherap. Onderz., Leiden, Netherlands). *Pharm. Weekbl.*, 1960, **95** (8), 236.—Sulphamerazine can be identified by dissolution of about 5 mg in 8 ml of ethanol and addition of 2 ml of saturated Cu acetate soln. in ethanol. After scratching the tube for 1 min. a brownish-grey turbidity is observed. Other sulphonamides yield different colours in this reaction. Sulphamerazine in (1 + 1) mixtures with other sulphonamides can be identified in this way. Succinylsulphathiazole, sulphamethizole and sulphadiazine interfere when present in a fivefold excess.

M. J. MAURICE

**5422. Quantitative determination of ethanol in pharmaceutical products by gas chromatography.** H. J. Wesselman (Eli Lilly & Co., Indianapolis, Ind.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (5), 320-322.—*Procedure*—Mix the sample with a known vol. of acetone as internal standard and apply 1 or 2  $\mu$ l through a pre-heater at 300° to a column (6 ft.  $\times$  0.25 in.) packed with 30% of polyoxyethylene glycol 400 on 30 to 60-mesh Chromosorb, operated at 100°, with He as carrier gas at a flow rate of 75 ml per min. A sample can be assayed in <30 min. with a coeff. of variation of <5%. The calibration curve should be checked daily. Result for tinctures, fluid extracts, elixirs and other products assayed by this procedure and by the method of the U.S.P. XV are compared.

A. R. ROGERS

**5423. Infra-red assay of chloroform in pharmaceutical products.** J. C. Souder and P. Deluca (Smith, Kline and French Lab., Philadelphia, Pa.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (4), 255-256.—Extract either the aq. sample or, if emulsifying agents are present, a distillate of the sample, with CS<sub>2</sub> and measure the i.r. absorptions of the extract at 13.17 and 12.5  $\mu$  in 0.01-cm cells. Calculate the concn. of CHCl<sub>3</sub> from the absorption difference. The coeff. of variation is  $\approx \pm 1\%$ .

A. R. ROGERS

See also Abstracts—5126, Assay of antibiotics. 5265, Chlor- and brom-tetracyclines in tetracycline. 5276, Determination of 3-deoxy sugars. 5289, Determination of barbituric and thiobarbituric acids. 5307, Determination of chloramphenicol. 5308, Gas chromatography of menthols. 5321, Determination of hexachlorophane. 5322, Chromatography of dyes used in pharmacy. 5389, Corticosteroids and their derivatives in biological fluids. 5392, Determination of anticholinesterases. 5453, 5454, 5455, 5456, 5457, 5458, 5459, 5460, 5461, 5462, 5463, 5464, 5465, Methods of determination of vitamins. 5481, Oleandomycin in feeding-stuffs. 5491, Chromatography of alkaloids and adrenals.

## Food

*Food and food additives, beverages, edible oils and fats, vitamins.*

**5424. Polarographic methods and their application to food analysis.** H. Woggon (Inst. f. Ernährung, Potsdam-Rehbrücke, Germany). *Ernährungsforschung*, 1960, **5** (2), 119-123.—A review with 22 references is presented. P. S. ARUP

**5425. Determination of aldehydes and ketones in foodstuffs. I. Micro-titration following treatment with 2:4-dinitrophenylhydrazine.** V. Hamann and A. Herrmann (Dtsch. ForschAnstalt f. Lebensmittel-Chemie, Munich). *Dtsch. LebensmittRdsch.*, 1960, **56** (4), 95-99; (5), 133-138.—The method is based on reaction of the carbonyl compounds with a standard soln. of 2:4-dinitrophenylhydrazine (I), followed by iodimetric titration of the excess of reagent. Satisfactory results were obtained in the analysis of essential oils and pure carbonyl compounds. *Procedure*—Dissolve the sample (15 to 25 mg) in ethanol or diluted ethanol (25 ml). Mix an aliquot of sample soln. (4 to 5 ml) with a 0.5% soln. of I in 2 N HCl (4 ml) and set aside for 1 hr., boil under reflux for 1 hr., cool in ice-water, dilute to 50 ml with water, and filter through glass wool and asbestos. To water (40 ml) add N Na acetate (3 ml), CHCl<sub>3</sub> (5 ml), 0.02 N iodine (5 ml) and finally an aliquot of sample filtrate (10 ml). Mix and set aside in the dark for 30 min., then titrate with 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (=a ml). A blank test is treated parallel with the sample (=b ml). Then carbonyl compound (%) =  $1.25(b - a)M/\text{sample weight}$ , where M = mol. wt. of carbonyl compound.

E. C. APLING

**5426. Dielectric determination of moisture in substances insoluble in dioxan. Application to sucrose and to refined sugar.** L. Cavallaro and L. Felloni (Ist. Chim., Univ. Ferrara). *Ind. Saccar. Ital.*, 1959, **52** (3-4), 57-67.—Moisture in sucrose is determined by measuring the increase in the dielectric constant of 1:4-dioxan, which is miscible with water, but which does not dissolve sucrose. The variations in the capacity of electric condensers are measured at  $25^\circ \pm 0.02^\circ$ , with a frequency of 1 MHz. The 1:4-dioxan is purified to remove all traces of water and acids. Any contact with moist air during the treatment must be avoided. The dielectric constant of the mixture varies linearly with the proportion of water. Results obtained with a refined sugar show good agreement with those obtained by the oven-drying method; results with commercial (not further purified) dioxan were similar but showed a greater spread, and it is then necessary to check the dielectric constant regularly. The accuracy of the method is  $\pm 0.01\%$ ; the time required for the analysis is 30 min. The literature of water determination is reviewed.

SUGAR IND. ABSTR.

**5427. Determination of moisture in sucrose by means of a high-frequency method.** G. Leonardi, E. Mariani and B. Rumi (Ist. Sup. della Poste e Telecom., Roma). *Ind. Saccar. Ital.*, 1959, **52** (3-4), 68-73.—An apparatus and method are described for the determination of water in sucrose by means of a high-frequency electrometric method, based on the variation of the dielectric constant of dioxan into which water from sucrose is extracted. The measuring cell, filled with the liquid to be tested, a variable condenser and two fixed condensers form



the arms of a capacitance bridge. Any changes in the capacity, and therefore the dielectric constant, are read from a micro-galvanometer, which is connected in parallel with two triodes and which gives a zero reading at equilibrium. The measuring cell consists of a double-walled Pyrex tube, the inner side of which is filled with mercury, which forms one electrode, the other electrode being an aluminium foil wound around the outer side. The intermediate space is filled with dioxan containing the water from the sucrose to be analysed. A circuit diagram is given, and the measuring apparatus, which is designed to exclude external moisture, is illustrated.

SUGAR IND. ABSTR.

**5428. Fractionation of sugars in beet molasses—fractional determination of raffinose.** N. Nunoko. *Proc. Res. Soc. Japan Sugar Refineries' Technologists*, 1959, **8**, 112-115.—Sucrose and raffinose in soln. (5 g and 0.4 g, respectively, in 100 ml of 5% ethanol) were separated by elution after adsorption on a column (3.5 cm × 25 cm) containing 25 g each of activated carbon and kieselguhr. Elution was carried out with 5% ethanol; 98% of the sucrose was recovered. Further elution with 15% ethanol gave a recovery of 0.3% of sucrose in the first two fractions, and 98.75% of the original raffinose was recovered in the next four fractions. Raffinose was also recovered from a beet-molasses sample containing 52.7% of sucrose and 5.4% of raffinose.

SUGAR IND. ABSTR.

**5429. Determination of the colour of pickled meat and meat products.** G. Gantner (Landesforschungsinstitut f. Fleischindustrie, Budapest). *Z. Lebensmittelforsch.*, 1960, **111** (4), 277-281.—The method of Hornsey (*J. Sci. Food Agric.*, 1956, **7**, 534; 1957, **8**, 547; 1959, **10**, 114) involving extraction of the sample with 80% aq. acetone is modified to overcome difficulties due to the rapid fading of the colour of the acetone extract on exposure to light, and to turbidity in the extracts from products containing much fat. The first is overcome by adding 0.5 ml of conc. HCl to the filtrate, shaking and setting aside for 10 min. The turbidity due to fat is prevented by adding 1 ml of trichloroethylene to 20 ml of the acidified acetone extract. After 10 min. the colour is measured in a Pulfrich photometer at 530 mμ. The method fails with products containing appreciable amounts of paprika.

C. L. HINTON

**5430. Composition of milk. III. Correlation between sodium, potassium, chloride and lactose contents of milk.** H. B. Praphulla and C. P. Anantakrishnan (Southern Reg. Station, Nat. Dairy Res. Inst., Bangalore, India). *Indian J. Dairy Sci.*, 1960, **13** (1), 24-28.—Statistical analysis of the results obtained on several hundred samples of cow and buffalo milk shows positive correlation between Na and Cl and between K and Cl contents, and negative correlation between Cl and lactose contents, for both cow and buffalo milk. A positive correlation exists between Na and K in cow milk, but not in buffalo milk. In all cases there was a highly significant positive correlation between milk yield and yields of Na, K, Cl and lactose.

E. C. APLING

**5431. Contribution to the analysis of butter and margarine in the ultra-violet.** L. Laporta (Lab. Chim. Provinciale, Pescara, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 156-160.—The spectrophotometric examination of 31 samples of

butter and 13 samples of margarine in hexane solution is reported and the marked differences in their u.v. absorption spectra are discussed.

E. C. APLING

**5432. Application of paper chromatography to differentiate ghee from other fats. II. Directly spotting fats on the chromatogram.** B. V. Ramachandra and N. N. Dastur (Southern Reg. Station, Nat. Dairy Res. Inst., Bangalore, India). *Indian J. Dairy Sci.*, 1960, **13** (1), 29-44.—A simple method for the detection of adulteration of ghee is described. The sample soln. (50% w/v in CCl<sub>4</sub>) is spotted 4 cm from the centre of an 18-cm Whatman No. 3 paper and irrigated with a mixture of 98% ethanol, isoamyl alcohol and CCl<sub>4</sub> (7:11:2). The volume of sample soln. taken is varied with the ambient temp. from 0.03 ml for temp. of 19° to 22° to 0.06 ml for temp. of 32°. Adulteration of ghee with 5% of buffalo-, goat- or sheep-body fat or 10% of vanaspati (hydrogenated arachis oil) causes obvious immobilisation of the fat spot, but adulteration with most vegetable oils is not detected. E. C. APLING

**5433. The amino acids of spirit vinegar. I. Detection of amino acids in spirit vinegar and in vinegar bacteria.** K. G. Bergner and H. R. Petri (Chem. Landesuntersuchungsanst., Stuttgart). *Z. Lebensmittelforsch.*, 1960, **111** (4), 319-333.—After high-vacuum concentration between 20.5° and 32° to avoid the Maillard reaction, amino acids were isolated from the concentrate by paper chromatography after passage through a cation exchanger (Amberlite IR-120H) followed, after elution with HCl and concentration of the eluate, by passage through an anion exchanger (Nalcite SAR OH). Eighteen amino acids were identified, all of which, except  $\gamma$ -aminobutyric acid, were found in the hydrolysate from the acetic acid bacteria used.

C. L. HINTON

**5434. Detection and determination of surface-active agents (Carbowax) in bread and similar products.** S. Anselmi, L. Boniforti and H. Monacelli (Ist. Sup. Sanità, Roma, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 278-279.—The proposed method is based on acid hydrolysis of the sample and pptn. of the extracted esters with 0.1 N iodine. *Procedure*—Mix the ground sample (15 g) with HCl (1:1) (25 ml) and immerse in a boiling-water bath for 10 to 15 min. Cool, and add carefully NaOH pellets (6 g) and heat again for 30 min. Cool, acidify with HCl (1:1), filter and evaporate the filtrate to dryness. Dissolve the residue with 95% ethanol (2 to 3 drops) and water (5 ml), and add, drop by drop, a 5% soln. of BaCl<sub>2</sub> in N HCl (5 ml), and then 0.1 N iodine. A ppt. varying in colour from brick-red to dark grey, according to the degree of polymerisation of the polyoxyethylene glycol present, forms immediately. Samples of bread containing olive oil, lard or butter, prepared in the laboratory without emulsifying agents, gave no ppt. The method can be made quant. according to the procedure of Anselmi *et al.* (*Anal. Abstr.*, 1960, **7**, 1578).

E. C. APLING

**5435. Chromatography and spectrophotometry of some permitted colours.** E. Miglietta (Lab. Chim. Provinciale, Brindisi, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 216-229.—*R<sub>F</sub>* values for ascending chromatography on Whatman No. 1 paper with four different solvent systems, and absorption spectra, are tabulated for 13 food colours.

Considerable differences in spectra and chromatographic behaviour are noted between different commercial samples of the same dye.

E. C. APLING

**5436. Determination of coal-tar colours on oranges.** W. Przybylski, R. B. Smyth and G. G. McKeown (Food & Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 274-278.—Synthetic dyes [mainly Citrus Red No. 2 and Oil Red XO (C.I. Solvent Orange 7)] were washed off the oranges with  $\text{CHCl}_3$ , the residue from its evaporation being dissolved in light petroleum. The dye was adsorbed on  $\text{Al}_2\text{O}_3$ , then eluted with ethanol, and its constituents were separated by paper chromatography and determined spectrophotometrically. A more rapid direct spectrophotometric procedure is suitable for the routine examination of Oil Red XO and Citrus Red No. 2 mixtures on oranges. Most samples contained  $\approx 1$  p.p.m. of total dye.

A. A. ELDRIDGE

**5437. Detection and determination of benzoic acid and methyl *p*-hydroxybenzoate in jams and non-alcoholic drinks by spectrophotometry.** R. Intonti, F. C. Ramusino and A. Stacchini (Ist. Sup. di Sanit., Lab. Chim., Roma). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 147-155.—The method depends on the interpretation of spectrophotometric measurements made at 226 and 255  $\text{m}\mu$  by means of simultaneous equations. For benzoic acid  $E_{1\%}^{1\text{cm}}$  is 753 at 226  $\text{m}\mu$  and 64 at 255  $\text{m}\mu$ , and for methyl *p*-hydroxybenzoate the values are 151 at 226  $\text{m}\mu$  and 990 at 255  $\text{m}\mu$ . The absorption curves of each preservative are unaffected by the presence of the other, whence benzoic acid (p.p.m.) =  $13.45E_{226} - 2.05E_{255}$  and methyl *p*-hydroxybenzoate (p.p.m.) =  $10.23E_{255} - 0.87E_{226}$ . Soln. suitable for spectrophotometric measurement are prepared by extraction of the sample (adjusted to pH 11) with ethyl ether to remove neutral and basic substances, followed by acidification and extraction of the preservatives with ethyl ether. The ether extract is washed with water, then evaporated to dryness, and the residue is dissolved in boiling water and diluted to a suitable volume for spectrophotometric measurement. Recoveries of added preservatives varied from 98 to 102%.

E. C. APLING

**5438. Behaviour of antibiotics in foods. I. Quantitative determination of antibiotics.** W. Diemair and W. Rödder (Univ. Inst. f. Lebensmittelchem., Frankfurt a.M.). *Z. Lebensmittelforsch.*, 1960, **111** (4), 265-277.—An agar diffusion test is described, suitable for measuring the activity of the tetracyclines, with *Bacillus subtilis* (ATCC 6633) as test organism. The spore suspension is added to the top layers of double-layer agar plates (prep. described). A series of dilutions of the test solution is prepared, aliquots (0.1 ml) of each being loaded on to two filter-paper discs on a test plate, a third disc being loaded with a standard reference soln. of chlortetracycline hydrochloride (I). A parallel series is run with dilutions of the standard. After incubation of the plates at 28° to 30° for 14 to 18 hr., the zones of inhibition are measured. The standard reference series gives a curve from which a correction factor can be applied to each plate. Residual activities are calculated for each dilution and averaged. The method is applied to the study of the stability of I in minced meat and milk.

C. L. HINTON

**5439. Determination of the chloramine value of fruit juices and preparations thereof.** E. Benk. *Riechstoffe u. Aromen*, 1960, **10** (4), 122-126.—Extensive tests show that the determination of the chloramine value is a very useful supplementary method for determining the fruit juice content of fruit juices, syrups, and drinks made therefrom, and for assessing their purity and freedom from adulterants. Adulterants generally lower the chloramine value considerably. Full discussions are given of the constituents and adulterants that react with the chloramine soln. during the determination. If alcohol and/or volatile additives, such as preservatives (e.g.,  $\text{SO}_2$ ) or aroma-producing compounds, are present they must be evaporated off before effecting the determination. *Procedure*—Filtered fruit juice (1 ml), syrup (1 g) or fruit drink (10 ml), after removal of any alcohol or volatile additive by evaporation, is mixed with 50 ml of 0.01 *N* chloramine T in a stoppered bottle, and set aside for 15 min. in the dark; solid KI and dil.  $\text{H}_2\text{SO}_4$  are added, and the liberated iodine is titrated with 0.01 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ . The difference (ml) between the vol. of chloramine soln. added and the vol. of  $\text{Na}_2\text{S}_2\text{O}_3$  soln. used gives the chloramine value.

H. L. WHITEHEAD

**5440. Carbohydrates in malting and brewing. IX. Rapid method for estimating the main carbohydrate constituents of worts.** G. Harris and I. C. MacWilliam (Brew. Ind. Res. Foundn., Nutfield, Surrey). *J. Inst. Brewing*, 1960, **66** (2), 147-150.—The principal oligosaccharides of wort, viz. sucrose, maltose, maltotriose and dextrans, can be individually estimated in a few hours by specific enzymic hydrolysis followed by measurement of the hexose formed by means of Barfoed's reagent. Commercial invertase is used together with two maltases from yeasts. Full details for the preparation of the enzymes and for the estimation are given.

C. A. SLATER

**5441. The reliability of the Rebelein index as a means of identification of genuine wines.** P. G. Garoglio (Ist. Ind. Agr., Univ. Firenze, Italy). *Ann. Sper. Agr.*, 1960, **14** (2), 267-291.—The Rebelein index,  $K = [\text{glycerol}]/[\text{butane-2:3-diol}]/[\text{ethanol}]^3$  (*Anal. Abstr.*, 1958, **5**, 700) has been calculated for a large number of Italian and Sicilian wines of known origin. The observed values of  $K \times 10^6$  varied from 2.1 to 9, whereas Rebelein regarded values of  $K \times 10^6 < 7$  as evidence of sophistication, and reported values from 7 to 9 for genuine German wines. In the examination of Italian wines, the index can only be of use for the detection of additions of alcohol sufficient to give values of  $K \times 10^6 < 2$ . The colorimetric determination of glycerol and butane-2:3-diol in wine is described (Rebelein, *Anal. Abstr.*, 1958, **5**, 701).

E. C. APLING

**5442. Investigation of hybrid red wines by chromatography of the colouring matter.** P. Jaulmes and —. Ney (Fac. Pharm., Montpellier, France). *Ann. Falsif.*, 1960, **53**, 180-183.—Conditions for the detection and rough quantitative determination of diglycoside in wines are recommended by a commission of the Service de la Repression des Fraudes. *Procedure*—Spots ( $2\text{ cm} \times 0.5\text{ cm}$ ) of 50  $\mu\text{l}$  of wine are placed 2 cm from the bottom of pieces of Arches 302 paper (or S. & S. 2043 bMgl) 20 cm long (machine direction). The spots are dried in a current of air at  $> 30^\circ$ , and chromatographed by the ascending technique in

a closed plastic vessel (25 cm high  $\times$  30 cm  $\times$  16 cm) with the sheets dipping 1 cm into a 2-cm layer of solvent [ $\text{H}_2\text{PO}_4$  (3.92 g) - glacial acetic acid (2.40 g) -  $\text{H}_2\text{BO}_3$  cryst. (2.48 g) made up to 1 litre with water and having a pH of 1.81]. The chromatogram is run for 17 cm ( $\approx$  2 hr.) and dried in air at 30°. The spots are examined in a dark room under u.v. light (366 m $\mu$ ) after exposure for 2 to 4 min. The distance of paper to lamp is adjusted until a spot of 1 mg per ml of ethanolic pinacyanol on the same kind of paper is visible, and one of half that concn. is invisible. The spot due to diglycoside has an  $R_F$  value of  $0.55 \pm 0.09$  and has a brick-red fluorescence. The chromatograms are preserved between black paper, the colour not being very stable. The most similar fluorescence is that due to pinacyanol, and the preparation of a reference scale with pinacyanol spots is described.

E. J. H. BIRCH

**5443. Infra-red spectroscopic characterisation of glycerides.** D. Chapman (Unilever Ltd., Port Sunlight, Cheshire). *J. Amer. Oil Chem. Soc.*, 1960, **37** (2), 73-77.—The i.r. spectra of a number of tri-, di- and mono-glycerides in their crystalline forms have been obtained. Samples were measured in liquid paraffin mulls or KCl discs or melted on rock-salt flats. The information obtained by these spectra is reviewed and discussed, with special reference to polymorphic form, chain length, type of unsaturation, and configuration of the glycerides.

R. A. HENDEY

**5444. The determination of the neutral oil content of crude vegetable oils.** R. B. R. Choudhury and L. K. Arnold (Iowa State Univ. of Sci. and Technol., Ames, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (2), 87-88.—The method is based on the silicic acid chromatographic method (cf. Borgstrom, *Acta Physiol. Scand.*, 1952, **25**, 101). *Procedure*—Shake 2 to 3 g of crude oil, 25 g of silicic acid, and 50 ml of  $\text{CHCl}_3$  in a 125-ml Erlenmeyer flask for 10 min. Filter through a sintered glass funnel under vacuum, and wash the silicic acid with five 50-ml portions of  $\text{CHCl}_3$ . Evaporate the combined  $\text{CHCl}_3$  extracts on a water bath. Dry to constant wt. at 105° in a vacuum oven or in an atmosphere of N. The phospholipid content of the crude oils can be determined by washing the silicic acid residues with methanol, followed by evaporation and weighing. The results for neutral oil in cottonseed, corn and soya-bean oils are in agreement with those obtained by the conventional chromatographic method.

R. A. HENDEY

**5445. Vapour-phase chromatography of fats. II. Technique employed and chromatograms of some vegetable and animal oils and fats.** S. Anselmi, L. Boniforti and R. Monacelli (Ist. Sup. Sanità, Roma, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 257-276.—Chromatograms showing the fatty acid composition of 5 different samples of olive oil and of 19 other vegetable and animal oils and fats are reproduced, and the technique used is described in detail. *Procedure*—Boil the sample (2 g) with methanol (35 ml) for a few minutes under a reflux condenser bearing a soda-lime tube. Add a 1% soln. of Na methoxide (3.5 ml) and continue boiling gently for 4 hr. Cool, dilute with water and extract the methyl esters with ethyl ether and light petroleum, and evaporate the extract to dryness. Evaporate the methyl esters (2 to 4  $\mu$ ) at 300° on to a column (2 metres  $\times$  4 mm) of Celite C22 charged with 25% of the polyester of succinic acid and ethanediol (prepared according to the method of

Craig and Murty, *J. Amer. Oil Chem. Soc.*, 1959, **36**, 549), and operated at 200°, with He as carrier gas at a rate of 2.5 litres per hr.

E. C. APLING

**5446. Ultra-violet spectrophotometric studies on olive oil.** V. Morani and C. M. Colloca (Staz. Chim.-Agr. Sper., Roma, Italy). *Ann. Sper. Agr.*, 1960, **14** (2), 293-307.—Spectrophotometric readings for soln. of oil (0.8 g) in ethanol (100 ml) at 262, 268 and 274 m $\mu$  are reported for a large number of oils of known origin, including edible pressed oils, acid and rancid oils, A and B rectified oils, and oils treated with hydrogen peroxide, superheated steam, decolorisers and neutralisers. Values of  $\Delta E = 1000[E_{262} - (E_{268} + E_{274})/2]$  range from +8 to -6 for virgin pressed oils, from +18 to +57 for acid and rancid oils, from +46 to +101 for A rectified oils, and from +100 to +240 for B rectified oils, but values of  $\Delta E$  are significantly altered by treatment of the oil and by the development of rancidity.

E. C. APLING

**5447. Modification of the Fitelson reaction.** G. P. Giannerini (Compartimentale Dogane e Imposte Dirette, Livorno, Italy). *Olivicoltura*, 1959, **14** (5), 12-13.—The Fitelson reaction for detecting tea-seed oil in olive oil was modified as follows. Prepare the tubes containing 1.5 ml of  $\text{CHCl}_3$  and 0.8 ml of acetic anhydride and cork them. For the analysis, add 4 drops of conc.  $\text{H}_2\text{SO}_4$  to each tube, cool, add 7 drops of oil, shake for 2 to 3 sec., and observe the colour (i) directly and (ii) after 1 hr. The colour changes are, for genuine olive oil green, to other shades of green; "Rettificato B," red to green in 1 to 2 min. (sometimes with orange, blue or purple discolorations), and finally to green; tea-seed oil, red only; mixtures of olive oil with 15 to 90% of tea-seed oil, orange - pink changing sometimes to green after several minutes, and finally orange - brown - green.

CHEM. ABSTR.

**5448. Determination of residual diazinon in olive oil.** M. Doretto (Chem. Lab., Ist. Sup. Sanit., Roma). *R.C. Ist. Sup. Sanit.*, 1960, **23** (3-4), 294-300.—Extract the oil (20 g) with *n*-hexane (40 ml) and 0.5 N NaOH (10 ml). Add satd. NaCl soln. (10 ml) to assist separation overnight. Centrifuge if necessary. Wash the hexane phase with 0.5 N HCl, add 48% HBr (5 ml), shake well, separate and transfer the aq. acid phase to a flask fitted with a reflux-condenser. Repeat the HBr extraction twice and pool the extracts. Hydrolyse by boiling for 2 hr. in a current of N, passing the liberated  $\text{H}_2\text{S}$  into 0.5% Zn acetate soln. (7 ml). Add to the Zn acetate soln. in rapid succession 0.1% *p*-aminodimethylaniline (0.5 ml) and 2% ferric chloride soln. (0.1 ml). A labile pink colour will be produced, followed, if diazinon be present, by a blue colour (methylene blue) reaching its max. intensity in 25 min. Make the vol. up to 10 ml and measure the extinction at 670 m $\mu$ . Correct for blanks done at least in duplicate on a known diazinon-free sample of the same type of oil. Calculate the amount of diazinon by reference to standard curves prepared in the same manner from pure or technical diazinon. The method gives results accurate to 0.5% for >0.5 p.p.m. of insecticide on 20 g of oil and >0.2 p.p.m. on 50 g of oil.

J. I. M. JONES

**5449. Determination of gallates in edible fats.** W. Cassidy and A. J. Fisher (County Hall, Taunton, Somerset, England). *Analyst*, 1960, **85**, 295-297.—The warm liquid sample (10 g) or 5 g of solid sample with 5 ml of liquid paraffin is shaken with 25 ml

of 95% methanol for 1 min. and then warmed in water at 40° to 45° for  $\approx$  15 min. The upper layer is separated and the extraction is repeated with 20 ml of methanol. The combined extracts are made up to 50 ml, 1 g of  $\text{CaCO}_3$  is added and the mixture is shaken for 30 sec. and filtered, the first few ml of filtrate being discarded. To 10 ml of the filtrate 1 ml of acetone and  $\approx$  10 mg of powdered  $(\text{NH}_4)_2\text{SO}_4$ - $\text{FeSO}_4$  are added and the mixture is shaken for 1 min. After 30 min. the extinction is measured at 580  $\text{m}\mu$  and multiplied by 0.622, 0.785 or 0.952, according as the ester present is *n*-propyl, *n*-octyl or *n*-dodecyl gallate, to give the gallate present in 11 ml of final soln. A convenient extraction tube is described.

A. O. JONES

**5450. Rapid volumetric determination of free and combined oleic acid.** M. Antonacci. *Chim. e Ind.*, 1960, **42** (4), 375-377.—A method of fat analysis is based on the reaction of  $\text{Ca}^{2+}$  with oleic acid or with alkali oleate, to form the corresponding insoluble salt. The excess of  $\text{Ca}^{2+}$  is then determined with EDTA (disodium salt) in the presence of murexide. The soap (10 ml) is shaken with  $\text{CaCl}_2$  soln. (1 g per litre of Ca) (10 ml), standardised with EDTA soln., and 10% KOH soln. (5 ml). The soln. is made up to 100 ml and titrated with EDTA. Full details of the calculations are given.

C. A. FINCH

**5451. Paper chromatography of saturated, unsaturated and hydroxy fatty acids.** V. P. Skipski, S. M. Arfin and M. M. Rapport (Sloan-Kettering Inst., New York, U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (2), 259-265.—Reversed-phase ascending chromatography of 1 to 100- $\mu\text{g}$  amounts is carried out on Whatman No. 1 paper impregnated with liquid paraffin and developed for 15 to 23 hr. at room temp. or for 7 to 10 hr. at 35° to 40° for more efficient separation. For normal saturated and unsaturated fatty acids ( $\text{C}_{14}$  to  $\text{C}_{24}$ ) development is with 95% acetic acid equilibrated with the liquid paraffin, but for more critical separation unsaturated fatty acids are eliminated by development with glacial acetic acid-30%  $\text{H}_2\text{O}_2$  (9:1). To separate hydroxy acids development is with 60 to 75% acetic acid, depending on chain-length. The fatty acids are detected by treating the chromatograms with aq. bismuth subnitrate soln. and, after washing, with aq. ammonium sulphide soln. Unsaturated acids are detected with a starch-iodine soln.  $R_F$  values for 11 fatty acids are given and the method is applied to the analysis of fatty acids isolated from the gluco- and galacto-cerebrosides of bovine tissues.

W. H. C. SHAW

**5452. Estimation of saturated fatty acids of a fat by bromination followed by urea adduction.** T. N. Mehta, M. S. Murty and P. M. Meshramkar (Laxminarayan Inst. Technol., Univ., Nagpur). *Indian J. Appl. Chem.*, 1959, **22** (5-6), 218-220.—In the procedure described, the mixed fatty acids (2 to 3 g) are brominated in ethereal soln., the excess of Br is removed, and the urea adducts of the saturated fatty acids are formed and filtered off, and the acids are recovered therefrom by hydrolysis with warm dilute acid. Results for the fatty acids from arachis, cottonseed and physic-nut oils agree well with those by the lead salt-ethanol method of Twitchell (*J. Ind. Eng. Chem.*, 1921, **13**, 806) and by the oxidation method of Hilditch and Priestman (*Analyst*, 1931, **56**, 354). Results are also given for castor and chaulmoogra oils. The recovered saturated acids are free from all traces of unsaturation.

O. M. WHITTON

**5453. Problems connected with the chemical determination of vitamins.** B. Gassmann (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 98-114.—Physical and chemical analyses are not related to the same functional groups or molecular structure as those responsible for the biological effects. Various methods are discussed and inadequacies pointed out. A diagram is given that shows a systematic approach to the various analyses necessary, and deals with the extraction, purification of the extract, measurement and calculation. The importance of calculating the emitted or adsorbed radiation of substances other than vitamins is stressed. The future development of analytical procedures for vitamins is discussed.

I. DICKINSON

**5454. Chemical determination of vitamin A and carotene.** W. Wodasak (Chem. u. Lebensmitt. Untersuchungsanstalt, Hamburg). *Nahrung*, 1960, **4** (2), 170-182.—Analytical details and procedures of the following methods are given—(i) reaction with antimony trichloride, (ii) reaction with 2:3-dichloropropan-1-ol, (iii) the conversion of vitamin A into anhydrovitamin A and the determination of the extinction of this compound and (iv) determination of the extinction of vitamin A.

I. DICKINSON

**5455. Method for the biological determination of vitamin D. (Prophylactic X-ray method.)** H. Ackermann (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 164-169.—Details of the method are given.

I. DICKINSON

**5456. Progress in the chemical determination of vitamin D.** J. Tiews (Inst. f. Physiol. u. Ernährung der Tiere, Univ., München). *Nahrung*, 1960, **4** (2), 156-163.—Recently developed methods are discussed and the following points are made. Maleic acid can be used to eliminate tachysterols. Advantages have been gained by the development of column partition chromatography and the introduction of dyes for the elimination of fluorescent vitamin-A decomposition products which cannot be separated chromatographically. Various analytical schemes are indicated suitable for materials rich in vitamin D. For the analyses of vitamin-enriched food and feeding-stuffs the biological determination is still preferred.

I. DICKINSON

**5457. Biological and microbiological methods for the detection of vitamins of the B complex.** H. Haenel (Inst. f. Ernährung, Potsdam-Rehbrücke, Germany). *Ernährungsforschung*, 1960, **5** (2), 189-204.—A review is presented with special reference to the inherent limitations of these techniques, and the precautions necessary in order to obtain reliable results. (35 references.)

P. S. ARUP

**5458. Microbiological detection of B vitamins. Methods used in routine analyses.** H. Haenel (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 116-139.—Micro-organisms that do not themselves synthesise certain vitamins, but rely on the nutrient medium to grow and to multiply, can be used for the detection of these vitamins. Methods which have been used and approved by the Inst. für Ernährung are compiled and discussed in detail. Working instructions are given for the detection of (i) thiamine with *Neurospora crassa* 9185, (ii)



vitamin B<sub>6</sub> (pyridoxol, pyridoxal, pyridoxamine) with *N. sitophila* 9276, (iii) riboflavin with *Lactobacillus casei* 7469, (iv) nicotinic acid with *Lb. arabinosus* 8014, (v) biotin with *Lb. arabinosus* 8014, (vi) vitamin B<sub>12</sub> with *Lb. leichmannii* 7830, (vii) folic acid with *Streptococcus faecalis* 8043, (viii) pantothenic acid with *Lb. arabinosus* 8014, (ix) vitamin B<sub>9</sub> with *Ochromonas malhamensis*, (x) thiamine with *Lb. fermentum* 9338 and (xi) thiamine with *Lb. viridescens* 12706. I. DICKINSON

**5459. Chemical determination of riboflavin in foods. (Lumiflavin method.)** B. Gassmann (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 140-142.—The sample, which should contain 15 to 100 µg of riboflavin, is weighed into a 300-ml flask, 150 ml of 0.1 N HCl is added and the flask is autoclaved at 121° for 30 min. After cooling the product to 45°, the pH is adjusted to 4.5 to 5.4 with 3.7 M Na acetate (5 to 7 ml), 2 g of diastase is added and the flask is incubated for 30 min. at 45°, then cooled to 20° and made up to 250 ml with H<sub>2</sub>O and filtered. Aliquots are shaken with CHCl<sub>3</sub> in the proportion of 1:1.5 and centrifuged. Portions (10 ml) of the aq. phase are pipetted into flat dishes. Standard soln. (2 ml = 2 µg of riboflavin) are added to half the number of dishes, and H<sub>2</sub>O (2 ml) to the other half. A slight excess of KMnO<sub>4</sub> soln. is added and removed after 1 min. with H<sub>2</sub>O<sub>2</sub>, then 2 ml of 7 N NaOH is added quickly with constant stirring. The samples are photolysed for 30 to 35 min. at 20° with a 500-watt lamp at 30 cm distance. The soln. are then acidified with 2 ml of glacial acetic acid, and 0.3 ml of 3% KMnO<sub>4</sub> soln. is added; after 1 min. the excess of KMnO<sub>4</sub> is removed with 0.3 ml of 1.7% H<sub>2</sub>O<sub>2</sub> soln. The contents of the dishes are transferred to centrifuge tubes, 30 ml of CHCl<sub>3</sub> is added, shaken and centrifuged. The aq. layer is pipetted off. The soln. is dried with Na<sub>2</sub>SO<sub>4</sub> and centrifuged again, and the fluorescence of the decanted soln. is measured. I. DICKINSON

**5460. Chemical determination of thiamine in food.** B. Gassmann (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 143-148.—Details of the thiochrome method are given. I. DICKINSON

**5461. Chemical determination of the antipellagra vitamin (total nicotinic acid) in food. (Cyanogen bromide method.)** B. Gassmann (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 149-152.—Details of the method are given. I. DICKINSON

**5462. Chromatographic separation of niacin (nicotinic acid) and its derivatives on a preparative scale using the ChroMax column.** C. Ovenfors (Royal Inst. of Technol., Div. of Food Chemistry, Stockholm, Sweden). *Sci. Tools*, 1960, **7** (1), 1-5.—Separation of 10-mg quantities of nicotinamide (I), nicotinic acid (II), N-methylnicotinamide (III), diphosphopyridine nucleotide (IV) and triphosphopyridine nucleotide (V) has been achieved by use of a ChroMax pressurized paper column (cf. Hagdahl and Lerner, *Ibid.*, 1958, **5**, 5). I and II were eluted with *n*-butanol-1.5 M aq. NH<sub>3</sub> (25:4), III with *n*-propanol-0.1 M phosphate buffer (pH 6.8) (4:1), and IV and V with *n*-propanol-phosphate buffer (11:9). I and II have also been separated in 500 to 1000-mg quantities. A. R. ROGERS

**5463. Application of cellulose ion-exchangers and alginic acid to the chromatographic purification and separation of the vitamins of the B<sub>12</sub> group.** J. Pawelkiewicz, W. Walerych, W. Friedrich and K. Bernhauer (Biochem. Inst. Landwirtschaftl. Hochschule, Poznań, Poland). *J. Chromatography*, 1960, **3** (4), 359-363 (in German).—The *R<sub>F</sub>* values for the vitamins on cellulose ion-exchangers, alginic acid and alginic acid-cellulose preparations are listed for solvent systems which consist of water and mixtures of water with various alcohols and of water with HCN. The method is very rapid and large amounts of the vitamins can be prepared. G. P. COOK

**5464. Comparison of some methods for the determination of ascorbic acid.** J. W. Haken (Lab. v. Tech. Landbouwhogeschool, Wageningen, Netherlands). *Chem. Weekbl.*, 1960, **58** (14), 205-206.—Five methods are compared, *vis.* (i) titration with 2:6-dichlorophenolindophenol, (ii) titration with iodine, with starch as indicator, (iii) potentiometric titration with iodine, (iv) paper chromatography by the method of Bergeret (*Anal. Abstr.*, 1959, **6**, 1120), and (v) conversion into the 2-nitrophenylhydrazide of oxalic acid followed by colorimetric determination (Moor, *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47**, 20). It is shown that method (iv) yields good results only when carried out by a highly skilled operator; methods (i), (ii) and (iii) give comparable results, (iii) having the highest precision. Method (v) is preferred, since it is more generally applicable, and its accuracy and precision are satisfactory. M. J. MAURICE

**5465. Chromatographic determination of ascorbic acid.** I. Crossland (Statens Vitamin Lab., Copenhagen, Denmark). *Acta Chem. Scand.*, 1960, **14** (4), 805-813 (in English).—Ascorbic acid (I) is freed from interfering impurities by chromatography on a cellulose column (40 cm long and 12 mm internal diameter), eluted with a mixture of EDTA, *n*-butanol, and aq. acetic acid, and determined in the eluate by measurement of the extinction at 570 mµ of the colour formed by reaction with diazotised nitroanisidine. Thus I (3 mg in 100 g of original sample) can be determined in metaphosphoric acid extracts of a variety of foodstuffs with an accuracy within ±2%. Apples contain an interfering substance. J. P. STERN

**5466. Chemical determination of vitamin C (ascorbic acid and dehydroascorbic acid) in food (combined method).** W. Feldheim (Dtsch. Akad. der Wissenschaften, Inst. für Ernährung Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 153-155.—Ascorbic acid is oxidised with excess of 2:6-dichlorophenolindophenol. The oxidation is stopped after 15 sec. and after 30 sec. by extraction of the excess of dye. The amount of the unused dye is determined photometrically. The dehydroascorbic acid contained in the aq. phase is determined together with the dehydroascorbic acid formed through oxidation, after both have been treated with 2:4-dinitrophenylhydrazine. Working instruction and analytical details are given. I. DICKINSON

**5467. Determination of total ascorbic acid by means of a suspension of *Erwinia solanicipra*. II. Specificity of the reduction of dehydroascorbic acid by these bacteria. Modification made in the technique of determination.** E. Géro and A. Candido (Lab. de Physiol. de la Nutr., Centre Nat. de la Rech. Sci., 16 rue de l'Estrapade, Paris, France). *Bull. Soc. Chim. Biol.*, 1960, **42** (4), 471-479.—When the

oxidised forms of substances interfering with the determination of ascorbic acid with 2:6-dichlorophenolindophenol are incubated with *Erwinia solaniasapra*, oxidised cysteine, glutathione, D-glucoscorbic acid and glucoreductone are not reduced by the bacteria; oxidised D-arabo-dehydroascorbic acid (which does not occur in natural media) is reduced, but much more slowly than dehydroascorbic acid. A carrot and potato broth which keeps for at least 5 months at room temp., and a synthetic medium for use as an alternative are described. The procedure for the determination of total ascorbic acid (Géro *et al.*, *Ibid.*, 1957, **39**, 1257) is modified by introducing a second pptn. with a mixture of 10% trichloroacetic acid and 10% metaphosphoric acid.

E. J. H. BIRCH

**5468. The course of reduction of dehydroascorbic acid by means of gaseous hydrogen sulphide related to pH range and time.** Z. Bozyk and S. Krauze (Dept. Bromatology, Med. Acad., Warsaw). *Roczn. Zchl. Hig.*, Warsaw, 1960, **11** (2), 143-155.—Published methods of reduction of dehydroascorbic acid (I) are discussed exhaustively. It is found that I is reduced quant. by means of gaseous  $H_2S$  in soln. of pH 6-7 during 15 min. The polarographic method for determining total I and ascorbic acid in fresh vegetables and fruits is satisfactory. B. K.

**5469. Chemical determination of vitamin E in foods. (Emmerie and Engel reaction.)** W. Feldheim (Dtsch. Akad. Wissenschaft., Inst. für Ernährung, Potsdam-Rehbrücke, Berlin). *Nahrung*, 1960, **4** (2), 183-185.—Details of the method are given.

I. DICKINSON

See also Abstracts—5126, Assay of vitamins. 5148,  $^{137}Cs$  in foods. 5272, Analysis of mono-glycerides. 5301, Chlorobenzenes in locusts. 5357, Flavanones in orange peel. 5374, Cystine in flour and beer. 5397, Riboflavin in tissues. 5480, Pesticide in olives.

### Sanitation

*Analysis of air, water, sewage, industrial wastes, industrial poisons.*

**5470. Improvements in or relating to apparatus for detecting and indicating the presence and amounts of carbon dioxide in an atmosphere.** H. T. Ringrose. Brit. Pat. 843,936; date appl. 17.7.56.—A pair of identical sealed porous vessels have the interior of one vessel connected to one arm, and the interior of the other vessel connected to the other arm of a manometer. A carton of moist soda lime is inserted in one vessel and a carton of cotton wool or other absorbent material, the hygroscopic properties of which have been increased by the deposition of or impregnation with  $CaCl_2$ , is inserted in the other vessel. Before insertion their respective vessels the vapour pressures in the cartons are allowed to equalise (*e.g.*, by storing them together in a sealed vessel), and will remain balanced in spite of changes in the external humidity, temp. or pressure; the  $CO_2$  is absorbed only by the soda lime. J. M. JACOBS

**5471. Sensitive method of detection and determination of carbon monoxide in an atmosphere.** P. Paulin (École de Méd et de Pharm., Tours, France). *Bull. Soc. Chim., France*, 1959, (11-12), 1845-1849.—The reduction of  $CoCl_2$  by  $As_2O_3$  is accelerated in the presence of CO, and it is shown that the time of appearance of reduced Au as a black ring on paper is inversely proportional to the cube root of the CO

concn. **Procedure**—A filter-paper (O.S.I. 7 kg per ream) is dipped in a soln. containing 2 g of  $KH_2PO_4$ , 0.1 g of  $Na_2HPO_4$  and 0.1 g of  $As_2O_3$  in 100 ml of water, and dried in air. (This impregnated paper keeps for only 1 month.) Before use, a drop of 2% gold chloride soln. (pH 1) is placed on the paper and, in the atmosphere to be investigated, the time taken for the black ring to appear is noted. Standard dilutions of CO are made by injecting the gas with a graduated syringe into a vessel of air. Interference by other gases which darken the paper ( $H_2S$ ,  $AsH_3$ , acetylene, aniline,  $SO_2$ , acetone and Hg vapour) or by acid vapours which delay the appearance of the ring is discussed. Some interference can be reduced by Chaignon's method, in which the paper is held between two plates of glass to exclude less rapidly diffusing gases. Interfering gases other than acetylene can be removed from the test sample by leaving it in contact with active carbon for 1 hr. Quantities of CO of the order of 1 in  $10^3$  can be detected with a time of appearance of the black ring of 115 sec. at 20° and 275 sec. at 5°. A rough estimation of the concn. of CO is possible.

E. J. H. BIRCH

**5472. Apparatus for electrically determining the concentration of hydrogen cyanide or hydrogen sulphide in air.** Mine Safety Appliances Co. [Inventor: H. H. Roth]. Brit. Pat. 841,548; date appl. 25.6.58.—The apparatus comprises an absorption chamber, within which a soln. of the compound to be determined is formed by passing a stream of the air to be tested through it, a cell including a calomel reference electrode connected by a salt bridge to a silver electrode over which the resulting soln. is made to flow, and means for effecting relative movement at high velocity between the silver electrode and the soln., *e.g.*, by rotating the electrode. The cell is connected electrically to suitable apparatus, *e.g.*, a millivoltmeter, for measuring the e.m.f. developed by the silver half-cell in the presence of cyanide ion (or  $H_2S$ ). J. M. JACOBS

**5473. Analysis of natural waters.** L. N. Podgornyi. USSR Pat. 126,656 (1.3.60).—Titrate the  $CO_3^{2-}$  and  $HCO_3^-$  in a sample with HCl, pass the soln. through a column of sulphonated polystyrene cationite resin (KU-2), and determine the total acidity in the filtrate, which is equivalent to the total cations. Determine Ca and Mg separately by titration with EDTA (disodium salt). Pass another sample of the water through the cationite without preliminary neutralisation of weak acids, and calculate the total strong acids from the total acidity of the filtrate. Determine  $Cl^-$  by Mohr's method, and  $SO_4^{2-}$  as the difference between total strong acids and  $Cl^-$ . In waters containing nitrates, phosphates and organic acids, determine  $SO_4^{2-}$  with EDTA (disodium salt); the difference between total acids and this result gives the total content of nitrates, phosphates and organic acids. To determine organic acids, pass the sample through the cationite, evaporate the soln. to dryness at 70° to 80°, dissolve the residue in 0.1 N NaOH, again pass the soln. through the cationite, and titrate with alkali to methyl orange. The EDTA (disodium salt) soln. is standardised against  $H_2SO_4$  by pptg.  $BaSO_4$  in the cold with a mixture of 0.2 N  $BaCl_2$  and 0.2 N  $MnCl_2$  and titrating the excess of Ba and Mn, or by pptg.  $BaSO_4$  with heating. C. D. KOPKIN

**5474. Determination of sodium and potassium in potable waters by flame photometry.** L. Olivari and R. Benassi (Lab. Chim. Provinciale, Reggio Emilia, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2),

230-239.—A rapid method for use with the Zeiss PQM/11 spectrophotometer is described. To minimise interferences, samples are acidified with conc.  $H_2SO_4$  (0.1 ml per 100 ml), 100 p.p.m. of  $Ca^{2+}$  is added to samples of low hardness, and standard curves for Na and K are prepared from soln. containing similar additions. Over a wide range of normal values of Na, K and Ca, the maximum error is  $\pm 1\%$ .  
E. C. APLING

5475. Complexometric determination of calcium and magnesium: the advantage of reverse titration. F. L. Hahn (Angel Urreza 718-303, Mexico City 12, D.F., Mexico). *Z. anal. Chem.*, 1960, **174** (2), 121-124 (in German).—The complexometric determination of hardness in water is discussed and advantages are claimed for the titration of a standard vol. of EDTA soln. with the water sample. The indicator recommended is a mixture of 1 part of Eriochrome black T and 0.2 part of methyl red, triturated with an equal amount of NaCl or  $Na_2SO_4$ . An error of less than 5% is claimed by this technique.  
T. R. ANDREW

5476. Determination of radium [in water]. A. V. D. Vloed. *J. Instn Wat. Engrs*, 1959, **13**, 601-604.—A method for the determination of Ra in water and in river mud and filter sand is described. A sample of water, previously acidified with  $HNO_3$ , is evaporated to decompose the organic complexes of Ra and permit the pptn. of silicates which are then removed by filtration in the case of river water or by centrifuging and filtration in the case of drinking water. The  $BaSO_4$  carrier is then pptd. from the nitrate soln., and the ppt., which contains both barium and radium sulphates, is heated, spread on a planchette, and the activity due to  $^{226}Ra$  is determined. Detailed procedure, and modifications for the analysis of sand and mud, are described.  
WAT. POLLUT. ABSTR.

5477. Determination of total carbon dioxide in water with complexans. P. Berbeni (Ist. Idrologia Medica, Univ. Pavia, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (2), 249-256.—The method depends on the pptn. of  $CO_2$  with a standard soln. of  $Ca(OH)_2$  and measurement of the excess of  $Ca^{2+}$  with standard EDTA soln. Procedure—Shake a measured vol. (v ml) of sample in a closed flask with a measured excess of standard  $Ca(OH)_2$  soln. [prepared by dissolving  $Ca(OH)_2$  (10 g) and  $CaCl_2 \cdot 6H_2O$  (0.2 g) in 1 litre of  $CO_2$ -free water] and set aside until clear. Titrate aliquots of the clear mixture, the water sample and the standard  $Ca(OH)_2$  soln. with 0.2 N EDTA (disodium salt). Then total  $CO_2$  (mg per litre) =  $22(B + b - A) \cdot 1000/v$ , where  $B$  = milli-equiv. of  $Ca^{2+}$  added as  $Ca(OH)_2$ ,  $b$  = milli-equiv. of  $Ca^{2+}$  in v ml of water sample, and  $A$  = milli-equiv. of  $Ca^{2+}$  found in the total volume of mixture. The maximum error is  $\pm 1\%$ .  
E. C. APLING

See also Abstracts—5287. Dimethylnitrosamine in air. 5303. Phenacyl chloride in air. 5486. Apparatus for O in air.

#### Agricultural analysis

Soil, fertilisers, herbicides, pesticides,  
animal feeding-stuffs.

5478. Removal of interfering ions in the determination of betaine in sugar-beet juices and plant material. A. Carruthers, J. F. Oldfield and H. J.

Teague (British Sugar Corporation Ltd., Bramcote, Nottingham, England). *Analyst*, 1960, **85**, 272-275.—The betaine soln. (10 ml) containing 1.5 to 7.5 mg per ml is passed through a column consisting of a mixture of De-Acidite FF (OH-form) (2 vol.) and Amberlite IRC-50 (H-form) (1 vol.). The percolate is collected and the column is washed with water until the total vol. is 50 ml. An aliquot acidified with HCl is treated with ammonium reineckate soln., the liquid is cooled to  $5^\circ$  and the pptd. betaine reineckate is collected in a sintered glass crucible and washed with ethyl ether. The ppt. is dissolved in 70% aq. acetone (10 ml) and water (10 ml), a soln. 0.1 N in both  $AgNO_3$  and  $NaNO_3$  is added, the liquid is filtered, the pptd. silver reineckate is washed with water and the betaine nitrate in the combined filtrate and washings is titrated with 0.01 N NaOH to methyl red. The method is applicable to aq. extracts of chopped plant material.  
A. O. JONES

5479. Infra-red spectrophotometric determination of isomers of hexachlorocyclohexane. C. Lupu and G. Stanescu. *Rev. Chim., Bucharest*, 1960, **11** (4), 232-235.—A modification of the Milone-Borello method (*Gazz. Chim. Ital.*, 1953, **83**, 255) is used, correcting for the errors due to the reciprocal influence of the isomers. Investigation of this method by comparison of standard curves made with pure  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - and  $\epsilon$ -isomers and synthetic mixtures showed that results were always high. For the  $\gamma$ -isomer, the error could be as high as +2%, a relative error of 15 to 25%. The extinction curves were drawn for each isomer in the presence of all the others in proportions varying within the percentages normally found in technical hexachlorocyclohexane (I). The effect of the  $\epsilon$ -isomer was ignored, since its normal content in the technical product is only  $\approx 1\%$ . Procedure—Technical I ( $\approx 0.5$  g) is dissolved in 10 ml of  $CS_2$ . This soln. is used for measuring the extinction with a Zeiss-Jena i.r. spectrophotometer and a 1.0-mm KBr cell for the  $\gamma$ -isomer at  $485\text{ cm}^{-1}$ , and for the  $\delta$ -isomer at  $567\text{ cm}^{-1}$ . The  $\alpha$ -isomer is determined in the same  $CS_2$  soln., with a 0.41-mm KBr cell, at  $507\text{ cm}^{-1}$ . The absorption of the  $\epsilon$ -isomer is read at  $547\text{ cm}^{-1}$ . For the  $\beta$ -isomer, a 0.25-mm NaCl cell is used, the reading being taken at  $743\text{ cm}^{-1}$ . These readings are referred to standard curves prepared from mixtures of the pure substances. The errors are claimed to be  $\pm 0.5\%$ .  
H. SHER

5480. Determination of residues of OO-dimethyl 8-methylcarbamoylmethyl phosphorodithioate [Rogor] in olives and various vegetable materials. B. Bazzi (Lab. di Signa, Ist. Ric. Agr., Firenze, Italy). Publ.: Soc. Gen. per l'Ind. Min. e Chem., Milano, 1960. 18 pp.—The main problem in the determination of residual amounts of the insecticide Rogor (I) is the extraction and purification of I in such a way as to allow of chemical, biological or spectrographic determination. Two procedures are described, the choice being governed by the ratio of I to oily matter. In the first, (i), the aliquot for analysis should contain  $>0.4$  to  $0.5$  g of oily matter and  $<3.5\text{ }\mu\text{g}$  of insecticide; in the second, (ii), the oily matter may be as much as 25 g. Preparation of sample—The material is pulped at  $>18^\circ$  with twice its wt. of  $CHCl_3$ . The mixture is filtered through cotton wool and centrifuged at  $>10^\circ$ . Procedure (i)—An aliquot (10 ml) of the clear extract is distilled at 0.5 torr in a boiling-water bath, to complete removal of the solvent. The

distillate is washed with  $\text{CHCl}_3$  into a Kjeldahl flask, the  $\text{CHCl}_3$  is evaporated off and organic matter in the residue is destroyed with 60%  $\text{HClO}_4$ . The phosphate in the residue is determined colorimetrically with ammonium molybdate. A blank prepared from untreated olives is carried out at the same time. *Procedure (ii)*—The  $\text{CHCl}_3$  from 200 ml of extract is removed in a Craig apparatus (*Anal. Chem.*, 1950, **22**, 1462) at 25° to 30° and the residue is dissolved in pentane. Insoluble matter is filtered off and the filtrate is chromatographed on an alumina column. Olive oil is washed out with pentane, and the adsorbed **I** is eluted with methyl cyanide. The methyl cyanide is removed in the Craig apparatus and the residue is transferred with ethyl ether to a micro-distillation apparatus, and treated as under (i). Recoveries of 92 to 98% were obtained with additions of 3.75 to 50  $\mu\text{g}$  of **I**. Comparative i.r. spectrographic and chromatographic studies with pure **I** showed that no changes are produced by the micro-distillation and other treatments. The sensitivity of (i) is 0.7 p.p.m. when 10 ml of extract and a 20-mm cell are used, and 0.4 p.p.m. with a 50-mm cell. The sensitivity of (ii) is 0.05 p.p.m. with 100 ml of extract. Reproducibility is good, the mean of 4 determinations of 1.5 p.p.m. added being  $1.39 \pm 0.06$ .

J. I. M. JONES

**5481. Determination of oleandomycin in animal feeds.** R. C. Kersey (Chas. Pfizer Co. Inc., Brooklyn, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (2), 211-213.—Oleandomycin was determined in animal feeds by a modification of Randall and Burton's method (*Ibid.*, 1957, **40**, 857). Details of the procedure are given and results tabulated. The collaborative study showed that the method is satisfactory.

A. A. ELDRIDGE

See also Abstracts—5392, Determination of anticholinesterases. **5448**, Residual diazinon in olive oil.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

**5482. Automatic recording electromagnetic balance.** K. A. Lincoln (U.S. Naval Radiological Defence Lab., San Francisco, 24). *Rev. Sci. Instrum.*, 1960, **31** (5), 537-539.—The balance is constructed from the movement of a 20-mA microammeter mounted so that the pointer is horizontal but moves in a vertical plane. The sample is attached to the end of the pointer which carries a small light bulb. Movement of the pointer affects the amount of light falling on an adjacent phototube which actuates a circuit feeding current to the milli-ammeter coil. The current required to restore the balance to zero is automatically recorded. The instrument operates over the range 0 to 100 mg with a precision of 0.04 mg, and is particularly suited for following rapid changes in weight, as in flash pyrolysis.

G. SKIRROW

**5483. Apparatus for routine analysis. V. An improved gas flowmeter.** G. Lindley (English Electric Co., Ltd., Bradford, England). *Lab. Practice*, 1960, **9** (4), 248.—In the apparatus described and illustrated, a wide range of flow rates is attained by interchangeable calibrated capillaries

or jets (mounted in rubber bungs or B7 cones) that can be inserted into the upper vessel, or alternatively by an adjustable orifice of the White-Wright type (*Canad. J. Res.*, B, 1936, **14**, 472). The design also provides adequate protection against sudden surges in the flow of gas. The apparatus is particularly useful for the determination of S in iron and steel.

W. J. BAKER

**5484. Estimation of efficiency for bubbler-type gas absorbers.** S. Calvert and W. Workman (Case Inst. of Tech., Cleveland, Ohio, U.S.A.). *Talanta*, 1960, **4** (2), 89-100 (in English).—Equations are developed which permit the estimation of the absorption efficiency of gas bubblers and give an indication of whether the system is subject to gas- or liquid-phase control. The factors affecting mass-transfer are discussed.

J. P. STERN

**5485. Gas-analysis apparatus [for use in physiological analyses of respired air].** B. B. Lloyd. Brit. Pat. 844,905; date appl. 25.4.58.—The apparatus comprises a gas burette, means for varying the pressure and available gas space within the burette, one or more absorption pipettes each comprising an absorption chamber and a reservoir chamber, the absorption chambers being adapted for connection to the burette in any desired sequence by means of a control tap with a multi-channel spigot. The reservoirs of the absorption liquids can be closed against the atmosphere so as to provide an enclosed vol. of gas above the liquid during an analysis.

J. M. JACOBS

**5486. A self-sampling indicator tube for oxygen.** B. E. Dixon and P. R. Kiff (Lab. of the Government Chemist, Clement's Inn Passage, Strand, London). *Talanta*, 1960, **4** (3), 203-205.—The apparatus, designed to measure the oxygen content of the atmosphere, consists of a sealed evacuated tube filled with a silica gel-manganous oxide mixture prepared *in situ*. When air is admitted by breaking the end of the tube, the oxygen content is determined from the lengths of changed (brown) and unchanged (green) material. A batch calibration curve is necessary. At ordinary pressure and temp., the results are reproducible within 5%. A correction formula is given for other pressures and temp. Since  $\text{CO}_2$  is absorbed by the first few cm of reagent, the oxygen content of  $\text{CO}_2$ -free air is given; if large amounts of  $\text{CO}_2$  are present, this must be determined separately.

R. M. S. HALL

**5487. A visual nephelometer.** V. N. Tsvetkov and V. S. Shaska. *Optics and Spectroscopy*, 1959, **7** (6), 474-476; English translation from *Optika i Spektroskopiya*, 1959, **7** (6).—A nephelometer, suitable for measuring the light-diffusing characteristics of solutions of compounds of high molecular weight, is described. For simplicity of design a visual photometer of the Pulfrich type is used in place of the photocell used in most other designs.

B. S. COOPER

**5488. Apparatus for counter-current extraction in the laboratory.** C. J. Asselbergs, J. F. Hengeveld, P. W. van der Poel and H. I. Waterman with H. W. Saeys and H. K. Kroeze. *Int. Sugar J.*, 1960, **62**, 95-97.—The construction of an apparatus designed for the extraction of sucrose from sugar beet is described.

N. E.

**5489. Studies on gel filtration. Sorption properties of the bed material Sephadex.** B. Gelotte (Res. Lab.,



Pharmacia, Uppsala, Sweden). *J. Chromatography*, 1960, **3** (4), 330-342 (in English).—Experiments on the bed material Sephadex G-25 (a cross-linked polysaccharide) were carried out with buffering substances, amino acids, purine and pyrimidine derivatives, vitamins, alkaloids and some simple aromatic substances. The bed material, in addition to the molecular sieve effect, gave a slight adsorption of aromatic and heterocyclic substances, but good recoveries were obtained in nearly all cases. A strong adsorption of some basic substances and a negative sorption of some acidic materials may occur, depending upon the ionic strength and the pH of the gel column but these effects are easily eliminated by the proper choice of experimental conditions. Sephadex does not appear to give irreversible adsorption and no detectable change in its properties occurs after prolonged use. G. P. COOK

See also Abstract—5315, Sulphur in petroleum products.

#### Chromatography, ion exchange, electrophoresis

5490. Time-saving applications in horizontal paper chromatography of amino acids. F. W. van Klaveren and G. Vaillancourt (Fischeres Res. Board of Canada, Tech. Sta., Grande-Rivière, Que.). *J. Chromatography*, 1960, **3** (4), 374-375 (in English).—A previous method (Chartier *et al.*, *Anal. Abstr.*, 1959, **6**, 1869) has been improved. The use of the solvent system *n*-butanol-ethyl methyl ketone-diethylamine-water (10:10:1:5) eliminates the need for re-chromatography, and a simple apparatus in which the spots are dried during the process of elution permits one operator to control six such procedures simultaneously. G. P. COOK

5491. Contributions to analytical chromatography. II. K. Teichert, E. Mutschler and H. Rochelmeyer (Pharm. Inst., J. Gutenberg Univ., Mainz, Germany). *Dtsch. ApothZtg*, 1960, **100** (11), 283-286.—The preparation of silica-gel and cellulose-powder plates (neutral or buffered), for use instead of chromatographic paper, is briefly described. In comparison with paper, the plates often require less time for development, and give sharper definition. Silica-gel plates, buffered at pH 6-8, can be used with advantage for the resolution of mixtures of primary and secondary amines (or their 3:5-dinitrobenzamides), of adrenaline and noradrenaline, and of theobromine, theophylline, caffeine and 4-aminophenazone. For the separation of the adrenalines, a little  $\text{Na}_2\text{S}_2\text{O}_8$  is added to the (Sörensen) buffer; as little as 0.005  $\mu\text{g}$  of either constituent can be detected. The alkaloid mixture can be developed in  $\approx 30$  min.; detectable amounts are  $< 1 \mu\text{g}$ . Cellulose-powder plates impregnated with formamide are very suitable for the resolution of the alkaloids of ergot; by the use of two successive solvents in the same direction, the ergotamine and ergotamine groups can be sharply separated in  $\approx 75$  min. Untreated cellulose plates can be used for the separation of mixtures of amino acids and of amines. Working details are given, including relevant  $R_F$  values and suitable solvents and reagents, for each of these procedures. P. S. ARUP

5492. Elatography. A special form of paper chromatography. A. Becker (CIBA A.-G., Basel, Switzerland). *Z. anal. Chem.*, 1960, **174** (3),

161-169 (in German).—The chromatographic separation of related compounds is frequently improved by the prior formation of derivatives. In "elatography," a band of reagent is applied to the paper and, as the sample traverses this area, derivatives are formed and the separation is improved. Examples given are the separations of aniline and *p*-toluidine, 2-naphthol-3:6-disulphonic acid and 2-naphthol-6:8-disulphonic acid, and reserpine and methyl reserpate; the detection of *p*-phenetidine, *p*-aminophenolsulphonic acid and *p*-aminophenol in *p*-phenetidinesulphonic acid, and of methyltestosterone in 1-dehydromethyltestosterone; and the determination of hydrazine in the presence of 1:4-dihydrazinophthalazine. T. R. ANDREW

5493. Statistical evaluation of the methods for measuring the curves obtained in gas chromatography. J. Janák (Czech. Acad. Sci., Brno). *J. Chromatography*, 1960, **3** (4), 308-312 (in German).—Seven geometrical and three automatic methods of measuring the curves obtained in gas chromatography were statistically evaluated from the results of about 100 analyses. The mean errors for areas of various sizes were determined. The conclusion reached is that the methods currently used are not yet quite satisfactory. G. P. COOK

5494. Ground unglazed tile—a new support for gas-liquid chromatography. V. Lukeš, R. Komers and V. Herout (Czech. Acad. Sci., Prague). *J. Chromatography*, 1960, **3** (4), 303-307 (in English).—Unglazed white tile, which has been ground to a grain size of 0.2 to 0.3 mm, is suitable for the separation of mono-terpene hydrocarbons (I) with tritoly phosphate (II) as the stationary phase. The maximum wettability of the support for II is 18% and the optimum amount for the separation of I is 7 to 10%. It has no catalytic effects on I, is mechanically very resistant, allows relatively high flow rates to be used and is easy to recover. G. P. COOK

5495. Stationary liquid phase for gas chromatography. Standard Oil Co. Brit. Pat. 844,424; date appl. 25.9.58. U.S.A., date appl. 27.9.57.—The stationary phase consists of safrole (1-allyl-3:4-methylenedioxybenzene) suspended on a column of inert ceramic packing. It is particularly suitable for the separation of  $\text{C}_5$  to  $\text{C}_8$  hydrocarbons at 80° F with He as carrier gas at 70 ml per min. J. M. JACOBS

5496. Radioassay by gas chromatography of compounds labelled with carbon-14. A. Karmen and H. R. Tricht (Lab. of Tech. Development, National Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1960, **186**, 150-151.—A device, consisting of short sections of column held at a lower temp. than the main column, is described for trapping materials from the effluent of a gas-chromatographic column to facilitate the collection of labelled components. It is also possible to obtain continuous scintillation counting in a single trap through which the column effluent flows. K. A. PROCTOR

5497. Ionisation detector for gas chromatography. A modification without radiation source. E. Haahti, T. Nikkari and E. Kulonen (Univ. Turku, Finland). *J. Chromatography*, 1960, **3** (4), 372-373 (in English).—Lovelock's detector (*Ibid.*, 1958, **1**, 35) can be used without a radiation source if it is constructed of glass. The characteristics of the response are the same as those of the  $^{90}\text{Sr}$  detector and the modified detector is especially useful for the analysis of the methyl esters of fatty acids. G. P. COOK

5498. Examination of scanning instruments used in electrophoresis. W. B. Yeoman (Frenchay Hosp., Bristol, England). *Clin. Chim. Acta*, 1960, **5** (2), 279-282.—A method of assessment of optical performance by means of photosensitive paper is described.  
H. F. W. KIRKPATRICK

### Optical

5499. Improved eyepiece graticule for measuring X-ray powder diffraction patterns. W. G. Perdok and G. Boom (Kristallograf. Inst., Univ. Groningen, Netherlands). *J. Sci. Instrum.*, 1960, **37** (4), 134-135.—Details, including a scale drawing, are given of a modification of the cross-wire system of the microscope which improves the accuracy of measurement of the Debye-Scherrer lines. The graticule is prepared by photographing a large-scale drawing.  
G. SKIRROW

5500. Displacement of the calibration curve through defocusing of the Littrow spectrograph. T. Torok and A. Petho (L. Eötvös Univ., Budapest). *Z. wiss. Photograph.*, 1959, **53**, 110-114.—Calibration curves used in evaluating concn. in routine spectrographic analysis must be re-checked from time to time. The new calibration curve is often displaced from the old one, the two running parallel to each other. Fluctuations in the light intensity and differences in the photographic material are among the reasons for the explanation of the phenomenon observed. Defocusing of the spectrograph is also important. The sharpness of the reference lines of a Littrow instrument is not constant. Owing to temp. variations, changes of the metal parts occur, resulting in a decrease of line sharpness. Experiments performed with calibration curves for the determination of Si, Cu and Fe in an aluminium alloy showed that, owing to displacement, the results for Si were 7% low. For Cu and Fe the error was 10 to 11%. The difference in the magnitude of the error can be explained through the ratio of the intensity and profile of the particular element line and the reference line.  
CHEM. ABSTR.

5501. Spectral analysis of solutions in a condensed spark with the help of a rotating spark electrode. W. Guttman (Potsdam-Rehbrücke, Berlin). *Chem. Tech., Berlin*, 1960, **12** (2), 77-81.—Solutions are sprayed into a spark discharge, which takes place between an electrode, concentric with, and rotating around, a stationary axially placed electrode. Photo-electric recording is used and the results obtained on standard soln. of Cd and Fe are compared with results from—(i) a previously used solution procedure, (ii) the Scheibe-Rivas method, and (iii) the rotating carbon disc method. The rotating spark procedure shows a significant increase in precision over the other techniques, whilst the 3 to 6% average accuracy obtained is comparable to that of the rotating carbon disc method.  
G. P. MITCHELL

5502. Spectrophotometry of dense light-scattering material. W. L. Butler and K. H. Norris (U.S. Dept. Agric., Beltsville, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **87** (1), 31-40.—Techniques applicable to the measurement of the visible-region absorption spectra of dense light-scattering samples are discussed and a single-beam, double-monochromator recording spectrophotometer suitable for this purpose is described. Practical aspects,

particularly the increase in effective path length due to scatter, are considered and a description is given of the application of the technique to the examination of cytochrome-*c* soln. containing  $\text{CaCO}_3$ , of yeast cells and of vegetable tissues and other materials.  
W. H. C. SHAW

5503. Flame spectrophotometer with spectrum recording and its use. N. S. Poluektov, S. B. Popova and L. A. Ovchar (Inst. of Gen. and Inorg. Chem., Acad. Sci. UkrSSR, Odessa). *Zhur. Anal. Khim.*, 1960, **15** (2), 131-137.—Working details are given of a recording flame spectrophotometer with recording of the spectra on paper. It is shown that this instrument has distinct advantages over ordinary spectrophotometers, taking as an example the determination of metals in the presence of other metals which give a complex spectrum in the region of the line to be measured photometrically. The determinations described in detail are Li in sodium chloride, Rb in the presence of predominant amounts of K, admixtures of Ca in strontium and rare earths, Sr in sea water and Mn in the presence of predominant amounts of K.  
A. BURWOOD-SMITH

5504. Heated vapour-absorption cell for infra-red spectroscopy. D. E. DeGraaf (H. M. Randall Lab. of Physics, Univ. Michigan, Ann Arbor, U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (4), 453-454.—The cell (diam.  $\approx 5$  cm) provides a sample path length of 7 cm. The brass cell body is provided with a vacuum valve and a sample reservoir. Double windows are held in position against O-ring gaskets. The cell is heated by insulated Chromel wire coils wound on each of two brass cylinders which fit over the ends of the cell. The cell, which fits into the sample space of a Perkin-Elmer spectrometer model 21, can be used at temp. up to  $180^\circ$  with a variation of  $<1^\circ$  over a period of 2 hr.  
G. SKIRROW

5505. Techniques for measuring the infra-red absorption spectra of fused salts. J. Greenberg and L. J. Hallgren (Minneapolis-Honeywell Res. Center, Hopkins, Minn., U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (4), 444-445.—Two methods have been applied for obtaining the i.r. absorption spectra of  $\text{NaNO}_3$  and  $\text{LiNO}_3$  in the solid and liquid phases. In the first method the sample is supported on a fine-mesh platinum screen. In the second method a reflectance cell is used in conjunction with the optics from the Perkin-Elmer reflectance attachment for the model-21 spectrophotometer. In both methods provision is made for preliminary purification of the salt and for temp. control and measurement. The measurements are made *in vacuo*.  
G. SKIRROW

5506. The use of selective radiation of gas in infra-red gas analysers. A. O. Sall' and S. V. Stanevich. *Optics and Spectroscopy*, 1959, **7** (2), 162-163; English translation of *Optika i Spektroskopiya*, 1959, **7** (2), 256.—A modified type of i.r. gas analyser is described in which the hot wire source of a conventional instrument is replaced by a heated cavity containing gas of the same nature as the constituent to be determined. The selective radiation of the heated gas is thus used in place of the continuous spectral radiation from a heated wire. It is claimed that this arrangement gives an increase in selectivity of the system as a whole.  
B. S. COOPER

**5507. Improved spectrofluorimeter for biochemical analysis.** D. W. Moss (Dept. of Clin. Path., Postgraduate Med. Sch., London, England). *Clin. Chim. Acta*, 1960, **5** (2), 283-288.—A description is given of an instrument having a correcting system to eliminate the effect of random fluctuations of light intensity. Some applications are given.

H. F. W. KIRKPATRICK

**5508. Photo-electric recording of Raman spectra excited by the 5875-A line of a helium lamp.** V. M. Pivovarov, L. A. Kirionova, Ya. S. Bobovich and G. N. Tarkhov. *Optics and Spectroscopy*, 1959, **7** (2), 163-164; English translation of *Optika i Spektroskopiya*, 1958, **7** (2), 258.—For coloured compounds it is often not possible to use the mercury line 4358 Å as the exciting radiation for Raman spectra. An alternative source is described, consisting of a spiral helium discharge lamp with cold cathodes, which emits the 5875-Å radiation at sufficient intensity for the satisfactory recording of Raman spectra by means of a large-aperture grating monochromator with photo-multiplier detector.

B. S. COOPER

**5509. Enhancement of the sensitivity of the optic-acoustic method of gas analysis by using cells with a multiple passage of radiation.** Ya. I. Gerlovin and P. V. Slobodskaya. *Optics and Spectroscopy*, 1959, **7** (1), 63-67; English translation of *Optika i Spektroskopiya*, 1959, **7** (1), 105.—The sensitivity of an i.r. gas analyser can be increased by the use of optical arrangements which bring about a multiple passage of radiation through the gas cells. It is shown that the increase of sensitivity depends on the reflection coeff. of the mirror and the astigmatism resulting from the optical design. Calculations are made to determine the optimum number of passages. The design of a multi-pass gas analyser is described.

B. S. COOPER

**5510. Colorimeter.** Technicon International Ltd. Brit. Pat. 846,171, date appl. 5.5.58. U.S.A., date appl. 5.6.57.—The flow cell of the colorimeter has a liquid chamber disposed in the path of light between a light source and a photo-electric device, and an inlet and outlet for the flow of a liquid through the chamber, whereby the response of the photo-electric device varies according to the light-absorption characteristics of the liquid. Means are provided for mounting the chamber in an adjustable position in the housing at the focus of the light source, and comprise complementary ball and socket parts on the flow cell and on integral parts of the colorimeter housing.

J. M. JACOBS

**5511. Differential method of photometric analysis. II. Application to solutions containing more than one component.** S. D. Ross and D. W. Wilson (Sir John Cass College, London, England). *Analyst*, 1960, **85**, 276-278.—The differential method previously applied to soln. containing single metals (*Ibid.*, 1960, **85**, 51) has been extended to two- and three-component systems containing the perchlorates of Ni, Cu, Co and Cr in the approximate proportions occurring in industrial alloys. Results for metal contents found in test systems by the proposed method are quoted. The mean error for two-component systems ranges from -0.39 to +0.35% and for three-component systems from -0.24 to +0.33%.

A. O. JONES

## Thermal

**5512. Glass combustion bomb.** R. L. Nuttall, M. A. Frisch and W. N. Hubbard (Chem. Engng Div., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (4), 461-462.—A glass combustion bomb which permits observation of rates of burning, sample melting, spattering, etc., has been constructed from standard commercial Pyrex-glass pipeline spacers held between stainless-steel end-plates and cushioned by Teflon gaskets. A normal stainless-steel bomb-head is sealed to the upper end-plate by an O-ring gasket. Safety screening consists of a wire screen surrounded by three concentric Lucite cylinders. Breaking pressure for a bomb of 3 in. internal diam. was about 1000 p.s.i.g.

G. SKIRROW

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K. A. PROCTOR

See also Abstracts—5222, Conductimetric apparatus. 5315, Apparatus for S in petroleum.



**5507. Improved spectrofluorimeter for biochemical analysis.** D. W. Moss (Dept. of Clin. Path., Postgraduate Med. Sch., London, England). *Clin. Chim. Acta*, 1960, **5** (2), 283-288.—A description is given of an instrument having a correcting system to eliminate the effect of random fluctuations of light intensity. Some applications are given.

H. F. W. KIRKPATRICK

**5508. Photo-electric recording of Raman spectra excited by the 5875-A line of a helium lamp.** V. M. Pivovarov, L. A. Kirionova, Ya. S. Bobovich and G. N. Tarkhov. *Optics and Spectroscopy*, 1959, **7** (2), 163-164; English translation of *Optika i Spektroskopiya*, 1958, **7** (2), 258.—For coloured compounds it is often not possible to use the mercury line 4358 Å as the exciting radiation for Raman spectra. An alternative source is described, consisting of a spiral helium discharge lamp with cold cathodes, which emits the 5875-Å radiation at sufficient intensity for the satisfactory recording of Raman spectra by means of a large-aperture grating monochromator with photo-multiplier detector.

B. S. COOPER

**5509. Enhancement of the sensitivity of the optico-acoustic method of gas analysis by using cells with a multiple passage of radiation.** Ya. I. Gerlovina and P. V. Slobodskaya. *Optics and Spectroscopy*, 1959, **7** (1), 63-67; English translation of *Optika i Spektroskopiya*, 1959, **7** (1), 105.—The sensitivity of an i.r. gas analyser can be increased by the use of optical arrangements which bring about a multiple passage of radiation through the gas cells. It is shown that the increase of sensitivity depends on the reflection coeff. of the mirror and the astigmatism resulting from the optical design. Calculations are made to determine the optimum number of passages. The design of a multi-pass gas analyser is described.

B. S. COOPER

**5510. Colorimeter.** Technicon International Ltd. Brit. Pat. 846,171, date appl. 5.5.58. U.S.A., date appl. 5.6.57.—The flow cell of the colorimeter has a liquid chamber disposed in the path of light between a light source and a photo-electric device, and an inlet and outlet for the flow of a liquid through the chamber, whereby the response of the photo-electric device varies according to the light-absorption characteristics of the liquid. Means are provided for mounting the chamber in an adjustable position in the housing at the focus of the light source, and comprise complementary ball and socket parts on the flow cell and on integral parts of the colorimeter housing.

J. M. JACOBS

**5511. Differential method of photometric analysis. II. Application to solutions containing more than one component.** S. D. Ross and D. W. Wilson (Sir John Cass College, London, England). *Analyst*, 1960, **85**, 276-278.—The differential method previously applied to soln. containing single metals (*Ibid.*, 1960, **85**, 51) has been extended to two- and three-component systems containing the perchlorates of Ni, Cu, Co and Cr in the approximate proportions occurring in industrial alloys. Results for metal contents found in test systems by the proposed method are quoted. The mean error for two-component systems ranges from -0.39 to +0.35% and for three-component systems from -0.24 to +0.33%.

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## ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current . . . . .	a.c.	milli-equivalent . . . . .	milli-equiv.
ampere . . . . .	amp.	milligram . . . . .	mg
Ångström unit . . . . .	Å	millilitre . . . . .	ml
anhydrous . . . . .	anhyd.	millimetre . . . . .	mm
approximate, -ly . . . . .	approx.	millimicrogram . . . . .	m $\mu$ g
aqueous . . . . .	aq.	millimolar . . . . .	mM
atmospher-e, -ic . . . . .	atm.	millivolt . . . . .	mV
boiling-point . . . . .	b.p.	minute (time) . . . . .	min.
British thermal unit . . . . .	B.Th.U.	molar (concentration) . . . . .	M
calorie (large) . . . . .	kg-cal.	molecul-e, -ar . . . . .	mol.
calorie (small) . . . . .	g-cal.	normal (concentration) . . . . .	N
centimetre . . . . .	cm	optical rotation . . . . .	$\alpha_D^t$
coefficient . . . . .	coeff.	ounce . . . . .	oz
Colour Index . . . . .	C.I.	parts per million . . . . .	p.p.m.
concentrated . . . . .	conc.	per cent. . . . .	%
concentration . . . . .	concn.	per cent. (vol. in vol.) . . . . .	% (v/v)
constant . . . . .	const.	per cent. (wt. in vol.) . . . . .	% (w/v)
crystalline . . . . .	} cryst.	per cent. (wt. in wt.) . . . . .	% (w/w)
crystallised . . . . .		potential difference . . . . .	p.d.
cubic . . . . .	cu.	precipitate (as a noun) . . . . .	ppt.
current density . . . . .	c.d.	precipitated . . . . .	pptd.
cycles per second . . . . .	c/s	precipitating . . . . .	pptg.
density . . . . .	$\rho$	precipitation . . . . .	pptn.
density, relative . . . . .	d or wt. per ml	preparation . . . . .	prep.
dilute . . . . .	dil.	qualitative, -ly . . . . .	qual.
direct current . . . . .	d.c.	quantitative, -ly . . . . .	quant.
distilled . . . . .	dist.	recrystallised . . . . .	recryst.
ethylenediaminetetra-acetic acid . . . . .	EDTA	refractive index . . . . .	$n_D^t$
electromotive force . . . . .	e.m.f.	relative band speed . . . . .	$R_F$
equivalent . . . . .	equiv.	relative humidity . . . . .	r.h.
gram . . . . .	g	revolutions per minute . . . . .	r.p.m.
gram-molecule . . . . .	mole	saponification value . . . . .	sap. val.
half-wave potential . . . . .	$E_{\frac{1}{2}}$	saturated calomel electrode . . . . .	S.C.E.
hour . . . . .	hr.	second (time) . . . . .	sec.
hydrogen ion exponent . . . . .	pH	soluble . . . . .	sol.
infra-red . . . . .	i.r.	solution . . . . .	soln.
insoluble . . . . .	insol.	specific gravity . . . . .	sp. gr.
international unit . . . . .	i.u.	specific rotation . . . . .	$[\alpha]_D^t$
kilogram . . . . .	kg	square centimetre . . . . .	sq. cm
kilovolt . . . . .	kV	standard temp. and pressure . . . . .	s.t.p.
kilowatt . . . . .	kW	temperature . . . . .	temp.
liquid . . . . .	liq.	ultra-violet . . . . .	u.v.
maxim-um, -a . . . . .	max.	vapour density . . . . .	v.d.
melting-point . . . . .	m.p.	vapour pressure . . . . .	v.p.
microgram . . . . .	$\mu$ g (not $\gamma$ )	volt . . . . .	V
microlitre . . . . .	$\mu$ l	volume . . . . .	vol.
micromole . . . . .	$\mu$ mole	watt . . . . .	W
micron . . . . .	$\mu$	wavelength . . . . .	$\lambda$
milliampere . . . . .	mA	weight . . . . .	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than . . . . .	>	less than . . . . .	<
not greater than . . . . .	$\nlessgtr$	not less than . . . . .	$\lessgtr$
is proportional to . . . . .	$\propto$	of the order of, approximately . . . . .	$\approx$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe<sup>II</sup>, Mo<sup>V</sup>. Substances in the ionic state are represented by Na<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, etc., for cations and by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, etc., for anions.

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